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# Relativistic nonadiabatic corrections to the ground state of molecular hydrogen



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# Relatywistyczne poprawki nieadiabatyczne w stanie podstawowym cząsteczki wodoru



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# Introduction

Chemistry and physics are sciences which are very closely intertwined. Quite often they investigate the same objects and processes, making the distinction somewhat artificial. The hydrogen molecule is a classic example of the common, interdisciplinary field between them. On the one hand, it has more than one nucleus, making it a molecule – a fully-fledged chemical entity. On the other,  $\text{H}_2$  is as simple as an electrically neutral molecule can be – simple enough to allow it to be investigated by fundamental methods typically too computationally demanding to be applied outside of physics.

Because of its simplicity, the hydrogen molecule was the first molecule investigated by means of quantum mechanics – becoming the cornerstone of quantum chemistry. As early as in 1927 – just two years after the modern quantum theory was formulated – Heitler and London applied it to  $\text{H}_2$  [1]. Their pioneering work showed how to implement the new theory to simple molecules, paving the way for the rapid development that followed. A summary of its first years can be found in a paper of Richardson [2] from 1935. From the results cited there, two deserve a particular mention: the dissociation energy of  $\text{H}_2$  ( $D_0(\text{H}_2)$ ) measured by Witmer (35000(1300)  $\text{cm}^{-1}$ ) [3] and its theoretical calculation by James and Coolidge (35970(160)  $\text{cm}^{-1}$ ) [4]. These numbers look very crude by today's standards<sup>1</sup>, but they are among the first results accurate enough for a meaningful comparison between theoretical and experimental spectroscopic data for  $\text{H}_2$ . Two other very important points on the timeline are 1960, when Herzberg and Monfils measured  $D_0(\text{H}_2)$  (36113.6(3)  $\text{cm}^{-1}$ ) [5], and 1968 – when Kołos and Wolniewicz accurately calculated that value to be 36117.4  $\text{cm}^{-1}$  [6]. Quite unexpectedly, the calculated total energy<sup>2</sup> of  $\text{H}_2$  was *more negative* than the experimental one – either a direct violation of the variational principle or a numerical error<sup>3</sup>. The latter possibility was very unlikely, as in fact Ref.

<sup>1</sup>It goes to show far the experimental and theoretical methods have gone since then.

<sup>2</sup>Related to the dissociation energy and energy of the hydrogen atom via  $E(\text{H}_2) = 2E(\text{H}) - D_0(\text{H}_2)$ .

<sup>3</sup>One could argue that the calculation included relativistic and radiative corrections [7, 8] – which

[6] involved recalculation of the previous results of Kołos and Wolniewicz [9, 10]<sup>4</sup>, using higher numerical precision and a larger basis set to expand the wave function. The conundrum was solved in 1970, when Herzberg repeated his measurement [11], and this time obtained a value consistent with the theory (he determined the upper bound of  $D_0(\text{H}_2)$  to be  $36118.3 \text{ cm}^{-1}$ ). In the same year, a measurement by Stwalley [12] followed, reporting a value of  $36118.6(5) \text{ cm}^{-1}$ . This meant not only that the theory was not wrong, but also that it helped to refine the experiment.

Since then, the experimental techniques have undergone impressive improvement [13, 14, 15], with a worthy mention of J. Hall and T. W. Hänsch, who were awarded the Nobel Prize in Physics in 2005 for their development of laser spectroscopy and the frequency comb technique. Currently, the most accurate experimental values for  $D_0(\text{H}_2)$  are  $36118.06962(37) \text{ cm}^{-1}$  [15] (J. Liu *et. al.*) and  $36118.06945(31) \text{ cm}^{-1}$  [16] (R. K. Altmann *et. al.*). To meet that level of accuracy on the theoretical side, we must employ computational methods going far beyond the approach typical for most quantum chemistry. Firstly, the Schrödinger equation for  $\text{H}_2$  has to be solved *very* accurately. Not only is its eigenvalue the greatest contributor to the total energy of the system, but also the eigenstate – the wave function – is needed, if the perturbation calculus is to be utilised to obtain further corrections. The equation can be solved either directly (e.g. Ref. [17]) or in the Born-Oppenheimer approximation [18]. If the latter approach is chosen, the nonadiabatic perturbation theory (NAPT) – described in detail in this thesis – can be employed to include the adiabatic and nonadiabatic effects. Independently of the method used to take it into account, the nonrelativistic theory alone is not sufficient when one is interested in such precision as we are. The problem was noticed in the mentioned works of Kołos and Wolniewicz, whose results included contributions from not only the relativistic, but also some of the quantum-electrodynamical (QED) effects. However, the theory has developed considerably since then [19, 20, 21, 22, 23]. To describe the relativistic and QED effects mentioned in a systematic and accurate way, we can use the so-called nonrelativistic quantum electrodynamics (NRQED) – which is covered in the next chapter.

By now, the most precise theoretical estimate of  $D_0(\text{H}_2)$  is  $36118.069632(26) \text{ cm}^{-1}$  [24] (Puchalski *et. al.*), which is in very good agreement with the experimental data referenced above. However, before that result was obtained, another notable disagreement between the theory and the experiment had occurred. In 2017, when the relativistic contribution to the total energy of rovibrational levels of  $\text{H}_2$  isotopomers was recalculated [23] (to increase the accuracy of the results available), the previously maintained theory-experiment agreement [25] was no more. The theoretical estimation of  $D_0(\text{H}_2)$  changed from  $36118.0691(6) \text{ cm}^{-1}$  [22] to  $36118.0678(6) \text{ cm}^{-1}$  [23], while the respective

means that the perturbation calculus is involved and the simple variational picture is distorted. However, those corrections are an order of magnitude smaller than the aforementioned discrepancy.

<sup>4</sup>They led to the  $D_0$  value of  $36117.3 \text{ cm}^{-1}$ , so in the new paper they actually made the disagreement even slightly *larger*.

experimental value was  $36118.06962(37) \text{ cm}^{-1}$  [15] at the time – a difference of several  $\sigma$ . For  $D_2$ , an analogous discrepancy was observed – theoretical  $36748.3614(4) \text{ cm}^{-1}$  [23] vs experimental  $36748.36286(68) \text{ cm}^{-1}$  [26]. The theory had to be completed somehow. The discrepancy was in general smaller in the heavier isotopomer,  $D_2$ , so a potential culprit was some finite-nuclear-mass effect. Because the fully nonadiabatic values for the nonrelativistic energy contributions had been already known at the time for many levels, the next possible suspect was the relativistic nonadiabatic contribution – the main topic of my thesis. It had previously been neglected, being mistakenly underestimated. Without spoiling the details yet – its inclusion proved to reconcile the theory and the experiment again, while also helping to further reduce the total uncertainty of the theoretical estimate of  $D_0(\text{H}_2)$  (and other rovibrational levels and transitions).

Comparison between theory and experiment can serve not only as a consistency check between them, but it can also potentially be exploited to determine such quantities and fundamental constants as the proton charge radius, electron-proton mass ratio, or the Rydberg constant  $R_\infty$  from molecular spectroscopy. For example, the proton charge radius  $r_p$  can be related to the dissociation energy of  $\text{H}_2$  via the following formula [24]

$$\frac{E(\text{H}_2, \text{IP})}{E(\text{H}, 2S-1S)} = \frac{E(\text{H}_2, \text{IP})_{(\text{point nucleus})}}{E(\text{H}, 2S-1S)_{(\text{point nucleus})}} - 1.4 \cdot 10^{-10} r_p^2 / \text{fm}^2, \quad (1.1)$$

where  $E(\text{H}_2, \text{IP})$  is the ionisation energy of molecular hydrogen and  $E(\text{H}, 2S-1S)$  is the  $2S-1S$  transition energy for atomic hydrogen. Currently,  $r_p$  is estimated from spectroscopic measurements for the hydrogen atom, but the scarcity of narrow transitions starts to be a limiting factor for the further increase in accuracy. The hydrogen molecule, with its wide array of rovibrational transitions with small natural width, backed by the above formula, presents an alternative way. The theoretically determined ionisation energy of  $\text{H}_2$  with assumed point nuclei, present in Eq. (1.1), depends on the accuracy of calculation of  $D_0$  for  $\text{H}_2$ . To obtain  $r_p$  with 1% precision, the accuracy of the calculation of  $D_0(\text{H}_2)$  has to be improved to the  $1.6 \cdot 10^{-7} \text{ cm}^{-1}$  level. The current agreement between the experimental and theoretical values of high accuracy gives us a reason to hope that such a level can be reached in the near future.

My thesis is aimed to be not only a presentation of the results I have obtained during my PhD studies, but also a relatively comprehensive review of the methods involved. The next two chapters provide an introduction to the theoretical approaches used: non-relativistic quantum electrodynamics (NRQED) and nonadiabatic perturbation theory (NAPT). The fourth chapter focuses on the main topic of the thesis – the relativistic nonadiabatic corrections to the energy of the hydrogen molecule, deriving the final formulas to be implemented and showing how to deal with certain problems along the way (nuclear gradients and singular operators). The fifth chapter describes the different basis set types that can be used to solve the electronic Schrödinger equation, the integrals that arise, and how to efficiently compute them. Different possible basis choices are discussed there – explicitly correlated exponential (ECE) functions, which I have researched during

my studies, in particular. The main result of my thesis – the relativistic nonadiabatic correction curve – is also presented in that chapter. The sixth chapter covers the methods to solve the nuclear Schrödinger equation, while also describing the current version of the `H2spectr` computer code developed by our research group. It is designed to be a ‘black box’ allowing the user to obtain the total energy (as well as its components) of any rovibrational level for any  $\text{H}_2$  isotopomer in the ground electronic state. The chapter also contains the numerical results of my thesis – the energies of chosen rovibrational transitions in  $\text{H}_2$ , HD,  $\text{D}_2$ , DT, and  $\text{T}_2$ , which are compared to available experimental data and discussed.

This is a second version of the thesis, updated with suggestions of the reviewers – for which they have my utmost gratitude. Moreover, I also took this opportunity to correct the mistakes I have been able to find since the submission of the thesis for the reviewing process, as well as to rephrase the sentences which I found unsatisfactory or confusing.



# NRQED

To maintain a similar level of accuracy as the current experiment, the theory needs to take into account the relativistic and QED effects. Although the formalism of QED is naturally well adapted to describe particle scattering processes, it is much harder to apply to the bound states – which the hydrogen molecule undoubtedly is. There are several different solutions to this problem (apart from the one described here, e.g. the two-time Green function method [27]). We are particularly interested in the so-called Nonrelativistic Quantum Electrodynamics (NRQED) [28]. In its effective Hamiltonian variant [29, 30], it provides a consistent means of relativistic and QED description of small chemical entities. Due to operating within the Schrödinger wave function formalism (and not Dirac bispinor), it can be systematically implemented over existing nonrelativistic calculation programs.

## 2.1 The formalism

The name *Nonrelativistic Quantum Electrodynamics* may require certain clarification – the electrodynamics describes photons, which are inherently *relativistic*. However, the other particles of which our system of interest comprises – electrons and nuclei – are not<sup>1</sup>. NRQED is an effective theory based on QED, crafted to the scale of nonrelativistic momenta of these massive particles [28]. The interaction carriers – photons – are integrated out and are not present in the final formulas of the theory. The leading energy contribution in such nonrelativistic systems is an expectation value of the Coulomb-Schrödinger Hamiltonian

$$H^{(2)} = - \sum_a \frac{\vec{\nabla}_a^2}{2m_a} + \sum_{a>b} \frac{q_a q_b}{r_{ab}}, \quad (2.1)$$

---

<sup>1</sup>At least unless electrons interacting with very highly charged nuclei are involved.

$$H^{(2)} |\Psi\rangle = E^{(2)} |\Psi\rangle, \quad (2.2)$$

where  $m_a$  is the mass of the  $a$ -th particle,  $q_a$  is its charge, and  $a, b$  iterate over all of the particles in the system (in  $\text{H}_2$ : 2 electrons and 2 nuclei). The method of approximate factorisation of this problem into the electronic and nuclear problems will be covered in the next chapter. All the other effects generate just small corrections to it, which allows us to treat them in a perturbative manner. NRQED assumes an expansion of the total energy in the fine-structure constant  $\alpha$

$$E(\alpha) = \alpha^2 E^{(2)} + \alpha^4 E^{(4)} + \alpha^5 E^{(5)} + \alpha^6 E^{(6)} + \alpha^7 E^{(7)} + \dots, \quad (2.3)$$

where  $E^{(n)}$  is a contribution of order  $\alpha^n m$ , with  $m$  being the electron<sup>2</sup> mass, and may include powers of  $\ln \alpha$ . On a sidenote – there are actually two conventions in literature: ‘physical’ and ‘chemical’, which differ by 2 in  $n$ . This is due to the way the rest mass  $mc^2 = m/\alpha^2$  is handled – in the ‘chemical’ notation, the nonrelativistic energy contribution is of the order  $\alpha^0$ , whereas in the ‘physical’ notation, assumed in the thesis, it is  $\alpha^2 m$ . To avoid confusion, in the latter the mass  $m$  is written explicitly, even though in the thesis the units where  $m = 1$  are ultimately assumed. In fact, in a system containing  $Z$ -charged nuclei, some terms are not proportional to  $\alpha^n m$ , but rather to  $(Z\alpha)^n m$ . It may lead to slow convergence when  $Z$  becomes large, and in such cases different expansion schemes have to be employed. This thesis is concerned with hydrogen molecule isotopomers ( $Z = 1$ ) only, so this problem will not matter here. What is noteworthy here, the  $E^{(n)}$  contributions are expectation values calculated just with a Schrödinger wave function – an eigenfunction of the Hamiltonian (2.1).

A convenient starting point for the calculations involving relativistic and QED effects is the Dirac Hamiltonian with an external field  $\vec{A}$

$$H_D = \vec{\alpha} \cdot \vec{\pi} + \beta m + eA^0, \quad (2.4)$$

where  $\vec{\pi} = \vec{p} - e\vec{A}$ ,  $e$  is the electron charge, and  $\vec{\alpha}$  and  $\beta$  are Dirac matrices

$$\alpha^i = \begin{bmatrix} 0 & \sigma^i \\ \sigma^i & 0 \end{bmatrix}, \quad \beta = \begin{bmatrix} \mathbb{I} & 0 \\ 0 & -\mathbb{I} \end{bmatrix}, \quad (2.5)$$

and where  $\sigma^i$  are Pauli matrices. There is a major problem associated with the Hamiltonian (2.4) – it is inherently one-body, so describing the interelectronic interactions in atoms and molecules with it is not straightforward. Should one construct a two-electron Hamiltonian by taking the Hamiltonian (2.4) for each of the two electrons and including a Coulombic electron-electron interaction naively, it would lead to the system having no stationary states – the so-called *Brown-Ravenhall disease* [31, 32]<sup>3</sup>. It is related to the fact that the spectrum of the Dirac Hamiltonian (2.4) comprises both positive and negative

<sup>2</sup>Or some other particle, e.g. a muon in muonic atoms/molecules.

<sup>3</sup>In Ref. [32] called *Brown-Ravenhall sickness*.

numbers, and its discrete subset is bounded by continuous intervals on both ends. For a many-body Hamiltonian constructed in the above manner (a so-called Dirac-Coulomb Hamiltonian), it means that the whole spectrum becomes continuous. This problem can be somewhat mitigated by a projection onto the space of positive-energy eigenstates of Eq. (2.4) – in practice done by a proper restriction of the basis set used in calculations [32]. However, such a restriction is not based on physical principles and adds a lot of ambiguity to the constructed theory. There lies a big advantage of QED – it describes these interactions in a field-theory manner, completely avoiding said *disease*.

The positive- and negative-energy eigenstates of the Dirac Hamiltonian (2.4) are coupled (through  $\vec{\alpha}$ ). Brown-Ravenhall disease aside, quite often (e.g. in the case of this thesis) we are interested in only one of these sets of solutions, but the coupling prevents us from simply discarding the other one. As usual, there are different methods of addressing this problem, often involving shifting of the energy scale and finding some approximate relations between negative and positive parts of the Dirac bispinors (see Refs [27, 32]). The Foldy-Wouthuysen (FW) transformation [33] is much more elegant and systematic though. It involves constructing a transformation of the Dirac Hamiltonian  $H_D$  into a new form  $H_{FW}$  where the negative- and the positive-energy solutions are decoupled

$$H_{FW} = e^{iS}(H_D - i\partial_t)e^{-iS}. \quad (2.6)$$

$S$  is chosen in such a way that  $H_{FW}$  does not contain odd operators<sup>4</sup>. There is some arbitrariness in the choice of  $S$ , and, in fact, it can be exploited to simplify the derivation. The standard approach is to perform several FW steps, each one increasing the accuracy by an order of  $1/m$  [33]. However, it is also possible to perform it in just one step if  $S$  could be chosen cleverly enough [30]

$$S = -\frac{i}{2m} \left\{ \beta \vec{\alpha} \cdot \vec{\pi} - \frac{1}{3m^2} \beta (\vec{\alpha} \cdot \vec{\pi})^3 + \frac{1}{2m} [\vec{\alpha} \cdot \vec{\pi}, eA^0 - i\partial_t] + Y \right\}, \quad (2.7)$$

where  $Y$  is an odd operator, such that  $[Y, eA^0 - i\partial_t] \approx [Y, (\vec{\alpha} \cdot \vec{\pi})^3] \approx 0$ , which is used in a later part of the derivation to cancel all the remaining odd terms of higher orders. In the next step,  $H_{FW}$  is expanded in powers of  $S$

$$H_{FW} = H_D + [iS, H_D - i\partial_t] - \frac{1}{2}[S, [S, H_D - i\partial_t]] - \frac{i}{6}[S, [S, [S, H_D - i\partial_t]]] + \dots, \quad (2.8)$$

up to the 6<sup>th</sup> order for the needs of the current theory [30]. Ultimately, the Foldy-Wouthuysen-transformed Hamiltonian reads [34]

$$\begin{aligned} H_{FW} = & eA^0 + \frac{\vec{\pi}^2}{2m} - \frac{\vec{\pi}^4}{8m^3} + \frac{\vec{\pi}^6}{16m^5} - \frac{e}{8m^2} \vec{\nabla} \vec{E} + \frac{5ie}{128m^4} [\vec{\pi}^2, \vec{\pi} \vec{E} + \vec{E} \vec{\pi}] \\ & + \frac{3}{64m^4} \{ \vec{\pi}^2, e \vec{\nabla} \vec{E} \} - \frac{e}{m} \vec{s} \vec{B} - \frac{e}{4m^2} \vec{s} (\vec{E} \times \vec{\pi} - \vec{\pi} \times \vec{E}) + \frac{e}{8m^3} \{ \pi^i, \{ \pi^i, \vec{s} \vec{B} \} \} \end{aligned}$$

<sup>4</sup>In this context *odd operators* – those that (like  $\vec{\alpha}$ ) couple the negative- and positive-energy solutions.

$$-\frac{e}{8m^3}\vec{\nabla}^2(\vec{s}\vec{B}) - \frac{e^2}{8m^3}\vec{B}^2 + \frac{3e}{32m^4}\vec{s}\{\vec{\pi}^2, \vec{E} \times \vec{\pi} - \vec{\pi} \times \vec{E}\} + \frac{e^2}{8m^3}\vec{E}^2, \quad (2.9)$$

where  $\pi^i$  is the  $i$ -th Cartesian coordinate of  $\vec{\pi}$  (and this convention is used consistently in the further part of the thesis, for other vectors). Decoupling the negative-energy solutions from the positive ones, possible thanks to the FW transformation, turns a Dirac bispinor problem into a Pauli spinor one (a four-component method into a two-component one). Having  $H_{FW}$ , one can, in a manner typical for quantum field theories, construct a Lagrangian

$$L = \Psi^\dagger(i\partial_t - H_{FW})\Psi + L_{EM}, \quad (2.10)$$

where  $\Psi$  is a nonrelativistic fermion (electron) field and  $L_{EM}$  is a Lagrangian of the electromagnetic field. All the NRQED energy corrections to the (many)electron propagator  $G(t - t')$  can be derived using the Feynman diagram approach with this Lagrangian [30, 35]. The Fourier transform in  $t' - t$  of such a propagator is

$$G(E) = \frac{1}{E - H^{(2)} - \Sigma(E)}, \quad (2.11)$$

where  $H^{(2)}$  is a nonrelativistic Schrödinger Hamiltonian (2.1) and  $\Sigma(E)$  entails all the additional relativistic/QED corrections

$$\Sigma(E) = \Sigma^{(4)}(E) + \Sigma^{(5)}(E) + \Sigma^{(6)}(E) + \dots, \quad (2.12)$$

with  $\Sigma^{(i)}(E)$  being of the  $i$ -th  $\alpha$  order. The bound state energy  $E$  can then be related to the position of the pole of the matrix element calculated with a *nonrelativistic wave function* [30]

$$\langle \psi | G(E) | \psi \rangle = \langle \psi | \frac{1}{E - H^{(2)} - \Sigma(E)} | \psi \rangle = \frac{1}{E - E^{(2)} - \sigma(E)}, \quad (2.13)$$

$$\sigma(E) = \langle \psi | \Sigma(E) | \psi \rangle + \langle \psi | \Sigma(E) \frac{1}{(E - H^{(2)})'} \Sigma(E) | \psi \rangle + \dots, \quad (2.14)$$

where the prime above denotes the omission of the state  $|\psi\rangle$  in the resolvent. The bound state energy  $E$  is then [34]

$$E = E^{(2)} + \sigma(E^{(2)}) + \sigma(E^{(2)}) \frac{\partial \sigma(E^{(2)})}{\partial E^{(2)}} + \dots \quad (2.15)$$

NRQED assumes, like other similar approaches, that  $E$  can be expanded in a series in the fine-structure constant – Eq.(2.3).

## 2.2 Leading relativistic correction

The first nontrivial term, as well as the key term for the thesis, is  $E^{(4)}$  – the leading relativistic contribution, of the order  $\alpha^4 m$ . It is the expectation value of the Breit-Pauli

Hamiltonian, which – for the hydrogen molecule in the  $^1\Sigma_g^+$  state<sup>5</sup> – takes the form [36]

$$\begin{aligned}
 H^{(4)} = \Sigma^{(4)}(E) = & - \sum_a \frac{p_a^4}{8m^3} - \sum_x \frac{p_x^4}{8m_x^3} + \frac{1}{2} \sum_{a,x} \frac{1}{m_x m} p_a^i \left( \frac{\delta^{ij}}{r_{ax}} + \frac{r_{ax}^i r_{ax}^j}{r_{ax}^3} \right) p_x^j \\
 & - \frac{1}{2m^2} p_1^i \left( \frac{\delta^{ij}}{r_{12}} + \frac{r_{12}^i r_{12}^j}{r_{12}^3} \right) p_2^j - \frac{1}{2} \frac{1}{m_A m_B} p_A^i \left( \frac{\delta^{ij}}{R} + \frac{R^i R^j}{R^3} \right) p_B^j \\
 & + \frac{\pi}{2} \sum_{a,x} \left( \frac{1}{m^2} + \frac{\delta_{s_x}}{m_x^2} \right) \delta^3(r_{ax}) + \frac{\pi}{m^2} \delta^3(r_{12}) + \frac{\pi}{2} \left( \frac{\delta_{s_A}}{m_A^2} + \frac{\delta_{s_B}}{m_B^2} \right) \delta^3(R),
 \end{aligned} \tag{2.16}$$

where  $a$  iterates over all the electrons (1 and 2) and  $x$  – over the nuclei ( $A$  and  $B$ ),  $m$  is the electron mass, and  $\delta_{s_x}$  depends on the nuclear spin:  $\delta_{s_x} = 0$  for  $s_x = 0$ ,  $\delta_{s_x} = 1$  for  $s_x = 1/2$ , and – by convention –  $\delta_{s_x} = 0$  for  $s_x \geq 1$ .  $\vec{R} \equiv \vec{r}_{AB}$  – and this notation will be used in the further parts of the thesis. The first two terms of Eq. (2.16) account for the relativistic ‘mass increase’<sup>6</sup>. The third, fourth, and fifth terms are called the Breit corrections (‘orbit-orbit coupling’ terms) and can be attributed to the relativistic retardation of the Coulomb potential [27]. The remaining contributions, proportional to the 3D Dirac  $\delta$ s, are contributed by the so-called contact terms. In fact, they describe two separate physical contributions: Darwin<sup>7</sup> and spin-spin interaction. In practice, even if the above Hamiltonian is used in the fully nonadiabatic approach (treating electrons and nuclei on an equal footing), the second and the last terms can be neglected – the second one being proportional to the very small  $1/m_x^3$  and the last one not only to  $1/m_x^2$ , but also to the nucleus-nucleus Dirac  $\delta$  (and it is *extremely* improbable to find the nuclei at the same spot<sup>8</sup>).

<sup>5</sup>In this (singlet) state all the electronic-spin-dependent terms vanish.

<sup>6</sup>It emerges as one of the terms in the expansion of the relativistic kinetic energy  $\sqrt{p^2 c^2 + m^2 c^4} \approx mc^2 + \frac{p^2}{2m} - \frac{p^4}{8m^3 c^2}$ .

<sup>7</sup>It represents a purely relativistic phenomenon of *zitterbewegung* – the ‘smearing out’ of particle positions [33].

<sup>8</sup> $\langle \delta^3(R) \rangle \sim 10^{-50} \alpha^3$  for the ground state of  $H_2$  [24].



## NAPT

At this point, one has to choose how the nuclei of the system are going to be described. In principle, there is no reason to treat them fundamentally differently than the electrons — they are just heavier particles with a positive electric charge. The exact wave function  $|\Psi\rangle$  (2.2) depends on both the electronic and nuclear coordinates. Expanding  $|\Psi\rangle$  in a basis which includes those coordinates on an equal footing is often called ‘the fully nonadiabatic approach’ because it takes into account the effects of the electronic-nuclear movement coupling (the nonadiabatic effects) exactly. It thus leads to more accurate results by default. The fully nonadiabatic approach is, in fact, successfully used in  $\text{H}_2$  description – not only on the nonrelativistic [17], but also the relativistic [36] and QED levels [24]. On the downside, as one could expect, the problem to solve is more complicated because all the particles are described at once. Moreover, that approach operates beyond the potential energy (hyper)surface (PES) concept. PES is a hypersurface constituted by all the possible geometrical configurations of the nuclei (which are fixed in space), with the corresponding energies of the system associated. It can be a very useful tool when studying chemical reactions or checking the stability of the numerical calculations (by investigating the PES for any suspicious irregularities). Additionally, PES, once calculated for a given electronic state, can then be reused to calculate all the possible rovibrational state energies for all the molecular isotopomers in that electronic state. It is a substantial advantage in theoretical infrared spectroscopy.

To both avoid the complexity of nonadiabatic calculations and retain PES, in chemistry usually the Born-Oppenheimer (BO) approximation is assumed. It splits the electronic and nuclear problems and solves them separately – one after the other. However, there is price to be paid because the nonadiabatic effects mentioned are completely neglected. Fortunately, there is a systematic way to reconcile these two – seemingly contradictory – worlds. This approach is called the *nonadiabatic perturbation method* (NAPT), and, unsurprisingly, it employs the perturbation method to split each  $E^{(n)}$  from Eq.(2.3)

further, into another series. This is the topic of this chapter – a case study of a hydrogen molecule isotopomer in the NAPT approach.

### 3.1 Nonrelativistic Hamiltonian

The movement of the whole molecule is not interesting from the point of view of its internal structure study, so we choose the centre-of-mass reference frame. As an added benefit, the four-particle problem becomes effectively a three-(quasi)particle one when the centre-of-mass movement is separated. The origin of the coordinate system is set to the geometric centre of the nuclei. Such a choice allows straightforward centre-of-mass separation and leads to relatively simple formulas, compared to some other possible choices<sup>1</sup>.

$$\vec{R}_C = \frac{1}{M}(M_A \vec{R}'_A + M_B \vec{R}'_B + \vec{r}'_1 + \vec{r}'_2), \quad (3.1)$$

$$\vec{R} = \vec{R}'_A - \vec{R}'_B, \quad (3.2)$$

$$\vec{r}_i = \vec{r}'_i - \frac{1}{2}(\vec{R}'_A + \vec{R}'_B), \quad (3.3)$$

$$M = M_A + M_B + 2. \quad (3.4)$$

The primes above denote coordinates in an arbitrary laboratory frame with the centre-of-mass not at rest, while the ones without the prime are expressed in the coordinate system described above.  $\vec{R}_C$  is the position of the centre-of-mass,  $\vec{R}_A$  and  $\vec{R}_B$  the position of the nuclei, and  $\vec{r}_1$  and  $\vec{r}_2$  the position of the electrons.  $M$  is the total molecular mass, and  $M_A$  and  $M_B$  are nuclear masses. The Schrödinger equation for the dinuclear, dielectronic molecule in such coordinates is

$$(H + H_n - E^{(2)}) |\Psi(\vec{r}_1, \vec{r}_2, \vec{R})\rangle = 0, \quad (3.5)$$

where

$$H = T + V, \quad (3.6)$$

$$T = -\frac{1}{2} \left( \vec{\nabla}_1^2 + \vec{\nabla}_2^2 \right), \quad (3.7)$$

$$V = -\frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}} + \frac{1}{R}, \quad (3.8)$$

$$H_n = -\frac{1}{2\mu_n} \left( \vec{\nabla}_R^2 + \vec{\nabla}_{\text{el}}^2 \right) + \left( \frac{1}{M_A} - \frac{1}{M_B} \right) \vec{\nabla}_R \vec{\nabla}_{\text{el}}, \quad (3.9)$$

and where 1, 2 indices again denote electrons, A, B denote nuclei, the nuclear reduced mass is  $\mu_n = M_A M_B / (M_A + M_B)$ , and  $\vec{\nabla}_{\text{el}} = (\vec{\nabla}_1 + \vec{\nabla}_2) / 2$ . Note that Eq. (3.9) contains a term that vanishes in homonuclear molecules, such as  $\text{H}_2$ .

<sup>1</sup>For example, a seemingly more natural choice, with the origin at the centre of mass, complicates the form of the potential energy operator, making it dependent on masses [32].



All the centre-of-mass-dependent terms in the Hamiltonian could be easily factorised out – there are no terms coupling the degrees of freedom of the centre-of-mass with the electronic or nuclear ones. However, such a straightforward factorisation is not always possible, for example when the relativistic effects are considered, or just in the presence of an external electromagnetic field [37]. As proven in Ref. [37], even in such cases there exists a transformation that allows such separation – at least with a very good approximation. Thus, the validity of the derivations provided in the thesis can be in principle extended to the situations where the molecule does not rest.

## 3.2 Perturbative approach

In chemistry, one often assumes that the wave function (2.2) can be approximately factorised into the electronic and nuclear functions

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}) \approx \psi(\vec{r}_1, \vec{r}_2)\chi(\vec{R}), \quad (3.10)$$

which are solutions of the electronic

$$H|\psi(\vec{r}_1, \vec{r}_2)\rangle = \mathcal{E}(R)|\psi(\vec{r}_1, \vec{r}_2)\rangle, \quad (3.11)$$

and the nuclear

$$\left[-\frac{\nabla_{\vec{R}}^2}{2\mu_n} + \mathcal{E}(R) - E^{(2,0)}\right]|\chi(\vec{R})\rangle = 0 \quad (3.12)$$

Schrödinger equations, which can be solved one after the other. The Hamiltonian (3.11) is known as the *clamped nuclei Hamiltonian* – because it assumes fixed positions of the nuclei. The problem (3.11) is a two-particle one, obviously even simpler to solve than the full three-particle problem (3.5). The nuclear equation (3.12) describes the nuclei moving (rotating and vibrating) in the presence of the ‘electronic potential’<sup>2</sup>  $\mathcal{E}(R)$ . That is why the corrections to  $\mathcal{E}(R)$  are referred to as ‘potentials’ in the later parts of the thesis. Together, these two simplified equations are known as the famous Born-Oppenheimer approximation and are crucial for quantum chemistry.

However, as straightforward as the above problem is, it is not the real one. The nuclear-electronic coupling (nonadiabatic) effects are clearly not present in the above model. To include them – still retaining the benefits of the BO approximation – the nonadiabatic perturbation theory (NAPT) was formulated systematically by Pachucki and Komasa [38, 39, 40, 41]. The approach starts with a modified Eq. (3.10), with the orthogonal remainder  $\delta\Psi_{\text{na}}(\vec{r}_1, \vec{r}_2, \vec{R})$  included [40].

$$\Psi(\vec{r}_1, \vec{r}_2, \vec{R}) = \psi(\vec{r}_1, \vec{r}_2)\chi_{\text{na}}(\vec{R}) + \delta\Psi_{\text{na}}(\vec{r}_1, \vec{r}_2, \vec{R}), \quad (3.13)$$

---

<sup>2</sup>This, optionally with some corrections added, is the PES mentioned earlier. Here, due to the simple structure of  $\text{H}_2$ , it is a *curve* rather than a surface.

$$\langle \delta\Psi_{\text{na}} | \psi \rangle_{\text{el}} = 0. \quad (3.14)$$

The symbol  $\langle \cdot | \cdot \rangle_{\text{el}}$  denotes integration over electronic coordinates only. To obtain the explicit formulas for the corrections, one plugs the wave function (3.13) into the full Schrödinger equation (3.5) and makes use of Eq. (3.11) to separate the equation [40]

$$\left[ (H - \mathcal{E}) + (\mathcal{E} + H_{\text{n}} - E^{(2)}) \right] |\psi\chi_{\text{na}} + \delta\Psi_{\text{na}}\rangle = 0, \quad (3.15)$$

which leads to

$$|\delta\Psi_{\text{na}}\rangle = \frac{1}{(\mathcal{E} - H)'} (\mathcal{E} + H_{\text{n}} - E^{(2)}) |\psi\chi_{\text{na}} + \delta\Psi_{\text{na}}\rangle. \quad (3.16)$$

The expression  $1/(\mathcal{E} - H)'$  used above is a reduced resolvent, with the following property

$$\frac{1}{(\mathcal{E} - H)'} |\psi\rangle = 0. \quad (3.17)$$

Hence, the formula for  $|\delta\Psi_{\text{na}}\rangle$  can be simplified to

$$|\delta\Psi_{\text{na}}\rangle = \frac{1}{(\mathcal{E} - H)'} \left[ H_{\text{n}} |\psi\chi_{\text{na}}\rangle + (\mathcal{E} + H_{\text{n}} - E^{(2)}) |\delta\Psi_{\text{na}}\rangle \right]. \quad (3.18)$$

To obtain the nuclear part of the wave function  $\chi_{\text{na}}(\vec{R})$ , Eq. (3.15) is used again. By multiplying it by  $\langle \psi |$ , integrating over electronic coordinates, and utilising (3.11), one obtains

$$\langle \psi | \mathcal{E} + H_{\text{n}} - E^{(2)} | \psi\chi_{\text{na}} \rangle_{\text{el}} = - \langle \psi | \mathcal{E} + H_{\text{n}} - E^{(2)} | \delta\Psi_{\text{na}} \rangle_{\text{el}}. \quad (3.19)$$

Obviously,  $H_{\text{n}}$  contains differentiation operators, which act on both  $|\psi\rangle$  and  $|\chi_{\text{na}}\rangle$ . Remembering about the orthogonality relation Eq. (3.14), as well as that  $\langle \psi | \vec{\nabla}_R | \psi \rangle = 0$  and  $\langle \psi | \vec{\nabla}_{\text{el}} | \psi \rangle = 0$  (for bound states), one can simplify the emerging formula into

$$(\mathcal{E} + \mathcal{E}^{(2,1)} + H_{\text{n}} - E^{(2)}) |\chi_{\text{na}}\rangle = - \langle \psi | H_{\text{n}} | \delta\Psi_{\text{na}} \rangle_{\text{el}}, \quad (3.20)$$

where  $\mathcal{E}^{(2,1)}$  is defined as

$$\mathcal{E}^{(2,1)}(R) = \langle \psi | H_{\text{n}} | \psi \rangle. \quad (3.21)$$

The essence of the NAPT method is basically using Eqs (3.18, 3.20) iteratively. Plugging Eq. (3.18) into Eq. (3.20) repeatedly, one obtains subsequent orders of approximation [40]

$$(\mathcal{E} + \mathcal{E}^{(2,1)} - E^{(2)}) |\chi_{\text{na}}\rangle = -(H_{\text{n}} + H_{\text{n}}^{(2)} + H_{\text{n}}^{(3)} + \dots) |\chi_{\text{na}}\rangle, \quad (3.22)$$

where

$$H_{\text{n}}^{(2)} |\chi_{\text{na}}\rangle = \langle \psi | H_{\text{n}} \frac{1}{(\mathcal{E} - H)'} H_{\text{n}} | \psi\chi_{\text{na}} \rangle_{\text{el}}, \quad (3.23)$$

$$H_n^{(3)} |\chi_{na}\rangle = \langle \psi | H_n \frac{1}{(\mathcal{E} - H)'} (\mathcal{E} + H_n - E^{(2)}) \frac{1}{(\mathcal{E} - H)'} H_n |\psi \chi_{na}\rangle_{\text{el}}, \quad (3.24)$$

and so on. Judging by the structure of the above formulas, they look like typical Rayleigh-Schrödinger corrections in  $H_n$ , with a notable complication that in NAPT here one has to carefully track the gradient operators acting on both  $\psi$  and  $\chi_{na}$ . This leads to increasingly complicated formulas for higher orders of the calculus. However, for the purposes of this thesis, no higher terms than  $H_n^{(2)}$  are included.

For homonuclear isotopomers<sup>3</sup>, the operator  $H_n^{(2)}$  can be reorganised into [40]

$$\begin{aligned} H_n^{(2)} = & \langle H_n \psi | \frac{1}{(\mathcal{E} - H)'} | H_n \psi \rangle_{\text{el}} + \frac{1}{\mu_n} \vec{\nabla}_R \langle \vec{\nabla}_R \psi | \frac{1}{(\mathcal{E} - H)'} | H_n \psi \rangle_{\text{el}} \\ & - \frac{1}{\mu_n} \langle H_n \psi | \frac{1}{(\mathcal{E} - H)'} | \vec{\nabla}_R \psi \rangle_{\text{el}} \vec{\nabla}_R - \frac{1}{\mu_n^2} \vec{\nabla}_R \langle \vec{\nabla}_R \psi | \frac{1}{(\mathcal{E} - H)'} | \vec{\nabla}_R \psi \rangle_{\text{el}} \vec{\nabla}_R. \end{aligned} \quad (3.25)$$

The additional terms which appear for heteronuclear isotopomers will be presented further. To simplify our formulation of NAPT, we can represent  $\chi(\vec{R})$  (and – analogously –  $\chi_{na}(R)$ ) as

$$\chi(\vec{R}) = \frac{\chi(R)}{R} Y_{Jm}(\theta, \phi), \quad (3.26)$$

where  $Y_{Jm}$  is a spherical harmonic. By such factorisation and subsequent integration over the angular coordinates  $\theta, \phi$ , the nuclear Schrödinger equation (3.12) becomes a radial nuclear Schrödinger equation – just an ordinary differential equation for  $\chi(R)$

$$H_N \chi(R) = E^{(2,0)} \chi(R), \quad (3.27)$$

$$H_N = -\frac{1}{2\mu_n} \frac{d^2}{dR^2} + \mathcal{E}(R) + \frac{J(J+1)}{2\mu_n R^2}, \quad (3.28)$$

where  $J$  is the rotational quantum number. Likewise, the  $H_n^{(2)}$  operator (3.25) can be written down as follows [40]

$$H_n^{(2)} = \mathcal{U}(R) + \left( \frac{2}{R} + \frac{d}{dR} \right) \mathcal{V}(R) - \frac{1}{R^2} \frac{d}{dR} R^2 \mathcal{W}_{\parallel}(R) \frac{d}{dR} + \frac{J(J+1)}{R^2} \mathcal{W}_{\perp}(R), \quad (3.29)$$

where [39]

$$\mathcal{U}(R) = \langle H_n \psi | \frac{1}{(\mathcal{E} - H)'} | H_n \psi \rangle_{\text{el}}, \quad (3.30)$$

$$\mathcal{V}(R) = \frac{1}{\mu_n} \langle \vec{n} \cdot \vec{\nabla}_R \psi | \frac{1}{(\mathcal{E} - H)'} | H_n \psi \rangle_{\text{el}}, \quad (3.31)$$

$$\mathcal{W}_{\parallel}(R) = \frac{1}{\mu_n^2} \langle \vec{n} \cdot \vec{\nabla}_R \psi | \frac{1}{(\mathcal{E} - H)'} | \vec{n} \cdot \vec{\nabla}_R \psi \rangle_{\text{el}}, \quad (3.32)$$

<sup>3</sup>For which the formula for  $H_n$  (3.9) does not contain the  $\left( \frac{1}{M_A} - \frac{1}{M_B} \right) \vec{\nabla}_R \vec{\nabla}_{\text{el}}$  term.

$$\mathcal{W}_\perp(R) = \frac{1}{\mu_n^2} \frac{\delta^{ij} - n^i n^j}{2} \langle \nabla_R^i \psi | \frac{1}{(\mathcal{E} - H)'} | \nabla_R^j \psi \rangle_{\text{el}}. \quad (3.33)$$

All  $\mathcal{U}$ ,  $\mathcal{V}$ ,  $\mathcal{W}_\parallel$  and  $\mathcal{W}_\perp$  can be found – as analytic fits – in Ref. [40]. Note the similar structure of Eqs (3.28, 3.29). In fact, it allows for the final form of the equation to be reorganised into [40]

$$\left[ -\frac{d}{dR} \frac{1}{2\mu_\parallel(R)} \frac{d}{dR} + \frac{J(J+1)}{2\mu_\perp(R)R^2} + \frac{\mathcal{W}'_\parallel(R)}{R} + \mathcal{Y}(R) \right] \chi_{\text{na}}(R) = E^{(2)} \chi_{\text{na}}(R) \quad (3.34)$$

where [40, 41]

$$\frac{1}{2\mu_\parallel(R)} = \frac{1}{2\mu_n} + \mathcal{W}_\parallel(R) - \lambda^2, \quad (3.35)$$

$$\frac{1}{2\mu_\perp(R)} = \frac{1}{2\mu_n} + \mathcal{W}_\perp(R) - \lambda^2, \quad (3.36)$$

$$\mathcal{Y}(R) = \mathcal{E}(R) + \mathcal{E}^{(2,1)}(R) + \delta\mathcal{E}_{\text{na}}(R) + \delta\mathcal{E}'_{\text{na}}(R), \quad (3.37)$$

$$\delta\mathcal{E}_{\text{na}}(R) = \mathcal{U}(R) + \left( \frac{2}{R} + \frac{d}{dR} \right) [\mathcal{V}(R) + \delta\mathcal{V}(R)]. \quad (3.38)$$

$\lambda$  and  $\delta\mathcal{E}'_{\text{na}}(R)$  are additional terms exclusive for heteronuclear molecules – introduced by the nonvanishing second term proportional to  $\vec{\nabla}_R$  in  $H_n$  (3.9)

$$\lambda = \frac{1}{2} \left( \frac{1}{M_A} - \frac{1}{M_B} \right), \quad (3.39)$$

$$\delta\mathcal{E}'_{\text{na}}(R) = \lambda^2 \left[ \langle \psi | \vec{\nabla}_R^2 + \frac{1}{2} r^i r^j \nabla_R^i \nabla_R^j (V) | \psi \rangle_{\text{el}} + \langle \psi | \vec{r} \cdot \vec{\nabla}_R (V) \frac{1}{(\mathcal{E} - H)'} \vec{r} \cdot \vec{\nabla}_R (V) | \psi \rangle_{\text{el}} \right], \quad (3.40)$$

where

$$\vec{\nabla}_R(V) = \frac{1}{2} \left( -\frac{\vec{r}_{1A}}{r_{1A}^3} + \frac{\vec{r}_{1B}}{r_{1B}^3} - \frac{\vec{r}_{2A}}{r_{2A}^3} + \frac{\vec{r}_{2B}}{r_{2B}^3} \right) - \frac{\vec{R}}{R^3}. \quad (3.41)$$

Their detailed derivation is presented in Ref. [41].

This is a good point at which to stress that NAPT is in general not equivalent to the expansion in powers of the electronic-to-nuclear-reduced-mass ratio  $m/\mu_n$ . Up to this point, these two coincided, but from the third NAPT order on, it is no longer true. For example,  $H_n^{(3)}$  contains not only terms proportional to  $(m/\mu_n)^3$ , but also a term proportional to  $(m/\mu_n)^2$  [40]. The thesis adapts the  $m/\mu_n$  expansion – up to the second order – so we have to include that additional contribution from  $H_n^{(3)}$  in Eq. (3.38)

$$\delta\mathcal{V}(R) = \frac{1}{2\mu_n^2} \frac{d\mathcal{E}}{dR} \langle \vec{n} \cdot \vec{\nabla}_R \psi | \left[ \frac{1}{(\mathcal{E} - H)'} \right]^2 | \vec{n} \cdot \vec{\nabla}_R \psi \rangle_{\text{el}}. \quad (3.42)$$

Eq. (3.34) is strikingly similar to the Born-Oppenheimer nuclear equation (3.27). The only differences are in PES ( $\mathcal{E}(R)$  vs  $\frac{\mathcal{W}'_{\parallel}(R)}{R} + \mathcal{Y}(R)$ ), and  $\mu_n$  now being replaced by terms dependent on the internuclear distance ( $\mathcal{W}_{\perp}(R)$  and  $\mathcal{W}_{\parallel}(R)$ ). In this way NAPT introduces the idea of ‘parallel/perpendicular reduced mass’, which, even more interestingly, depends on  $R$ . As unconventional as it may sound, it is simply due to the specific way of collecting terms by common factors and obviously has nothing to do with actual masses changing.

### 3.3 NRQED and NAPT combined

Combining NRQED and NAPT expansions together, one can obtain a 2D series – the energy expanded both in  $\alpha$  and  $m/\mu_n$ . It can be represented elegantly as a graph shown below. The following section covers the current status of the knowledge about its components for  $H_2$ .

	$\alpha^2 m$	$\alpha^4 m$	$\alpha^5 m$	$\alpha^6 m$	$\alpha^7 m$
$\left(\frac{m}{\mu_n}\right)^0$	$E^{(2,0)}$	$E^{(4,0)}$	$E^{(5,0)}$	$E^{(6,0)}$	$E^{(7,0)}$
$\left(\frac{m}{\mu_n}\right)^1$	$E^{(2,1)}$	$E^{(4,1)}$			
$\left(\frac{m}{\mu_n}\right)^2$	$E^{(2,2)}$				

Figure 3.1: Corrections to  $H_2$  energy. The dark blue squares represent the contributions known at the time of writing this thesis, the light blue – the contributions the knowledge of which is incomplete, the red one is the main result of the author's work.

#### Nonrelativistic BO contribution $E^{(2,0)}$

The nonrelativistic Born-Oppenheimer contribution to the energy  $E^{(2,0)}$  is the starting point of the 2D perturbation calculus – the unperturbed energy. The formulas for it have already been provided (3.11, 3.27, 3.28) in the previous section, but – for sake of systematicity – are shown here again

$$H |\psi(\vec{r}_1, \vec{r}_2)\rangle = \mathcal{E}(R) |\psi(\vec{r}_1, \vec{r}_2)\rangle, \quad (3.43)$$

$$H_N \chi(R) = E^{(2,0)} \chi(R), \quad (3.44)$$

$$H_N = -\frac{1}{2\mu_n} \frac{d^2}{dR^2} + \mathcal{E}(R) + \frac{J(J+1)}{2\mu_n R^2}. \quad (3.45)$$

Calculation of  $E^{(2,0)}$  is the natural point at which the choices of a numerical method and a basis set to expand the wave function have to be made. In general, in quantum chemistry it can be a major dilemma – due to the number of electrons of the system which can be significant. Among many methods, the following three: Configuration Interaction (CI), Coupled Cluster (CC), and – especially for large organic molecules – Density Functional Theory (DFT), are probably those which are the most commonly used (confer Refs [32, 42]). All of them either expand on the Hartree-Fock (HF) method (CC, CI) or utilise its numerical framework (DFT). This means that they employ one-electron basis functions, almost exclusively Gaussian – due to easy extensibility of integration algorithms.

Here however, in  $H_2$ , thanks to its simplicity, we can afford the very best – in terms of accuracy – methods available. It is possible to completely forget about the one-electron approximation and use the explicitly correlated sets in their various forms (not necessarily Gaussian), which will be covered in Chapter 5. Thanks to this,  $E^{(2,0)}$  can be evaluated with virtually any precision needed – typically as many as 13–19 significant digits can be achieved for the whole PES [18, 43].

### Nonrelativistic adiabatic contribution $E^{(2,1)}$

The adiabatic correction has already appeared in the section with derivation of the NAPT formalism. It is the term which makes the difference between BO and adiabatic theories, defined as in Eq. (3.21)

$$\mathcal{E}^{(2,1)}(R) = \langle \psi | H_n | \psi \rangle. \quad (3.46)$$

In fact, this is just the adiabatic correction to the PES. To obtain the contribution to the total molecular energy (including the energy of moving nuclei), two possible paths can be followed. First, one can just include  $\mathcal{E}^{(2,1)}(R)$  in the electronic potential present in the nuclear equation

$$\left[ -\frac{1}{2\mu_n} \frac{d^2}{dR^2} + \mathcal{E}(R) + \mathcal{E}^{(2,1)}(R) + \frac{J(J+1)}{2\mu_n R^2} - E_a^{(2)} \right] \chi_a(R) = 0, \quad (3.47)$$

with  $E_a^{(2)}$  being the adiabatically-corrected energy of a rovibrational state. Eqs (3.43, 3.46, 3.47) together are known as the adiabatic approximation (e.g. Ref [32]).

The other approach relies on further use of the perturbation calculus.  $\mathcal{E}^{(2,1)}(R)$  is treated as a first-order perturbation

$$E^{(2,1)} = \langle \chi | \mathcal{E}^{(2,1)}(R) | \chi \rangle, \quad (3.48)$$

with  $\chi$  being the BO radial function – the solution of Eq. (3.44). For comparison, for the  $D_0$  dissociation energy of  $H_2$  in the ground state (electronic and rovibrational), the first method (3.47) yields an energy different from the BO one by  $E_a^{(2)} - E^{(2,0)} = 5.7709817(3)$

$\text{cm}^{-1}$  [44], whereas the second one gives  $E^{(2,1)} = 5.76539989 \text{ cm}^{-1}$ . The difference,  $-0.0055818 \text{ cm}^{-1}$ , can be reproduced by adding further terms to  $E^{(2,1)}$ , beginning with the second-order

$$\langle \chi | \mathcal{E}^{(2,1)}(R) \frac{1}{(E^{(2,0)} - H_N)'} \mathcal{E}^{(2,1)}(R) | \chi \rangle = -0.0055827 \text{ cm}^{-1}. \quad (3.49)$$

However, it means that, in fact,  $E_a^{(2)}$  is ‘contaminated’ by contributions of all orders of  $m/\mu_n$  – introduced by the higher-order corrections. It causes certain ambiguity in the nomenclature. One can notice here that this is a more general problem, because all the contributions presented in this section can be taken into account either in the manner of Eq. (3.47) – by adding them to the  $\mathcal{E}(R)$  potential, or perturbatively, as in Eq. (3.48). This is one of the reasons why the main topic of the thesis, the nonadiabatic relativistic correction, is called a ‘(leading) nonadiabatic’, rather than ‘adiabatic’ – to avoid possible terminology clash. In the thesis, the perturbative approach is used consequently, except for the  $E^{(2,2)}$  contribution (see the next section).

The most accurate result to date for  $E^{(2,1)}$  for  $\text{H}_2$  is given in Ref. [44]. Actually, the result provided there is not for  $E^{(2,1)}$  (3.48), but rather for  $E_a^{(2)}$  (3.47). However, the work also presents the correction to the potential,  $\mathcal{E}^{(2,1)}(R)$  (both as a grid and an analytic fit), so the correction  $E^{(2,1)}$  can be easily evaluated too.

### Nonrelativistic nonadiabatic contribution $E^{(2,2)}$

Unlike  $E^{(2,1)}$ , direct calculation of  $E^{(2,2)}$  is not particularly convenient. Moreover, in the thesis we are ultimately interested in the total  $\alpha^2 m$  energy contribution, so instead we follow Eq. (3.34), repeated here below

$$\left[ -\frac{d}{dR} \frac{1}{2\mu_{\parallel}(R)} \frac{d}{dR} + \frac{J(J+1)}{2\mu_{\perp}(R)R^2} + \frac{\mathcal{W}'_{\parallel}(R)}{R} + \mathcal{Y}(R) \right] \chi_{\text{na}}(R) = E^{(2)} \chi_{\text{na}}(R) \quad (3.50)$$

where  $\mu_{\parallel}(R)$ ,  $\mu_{\perp}(R)$ ,  $\mathcal{W}'_{\parallel}(R)$ , and  $\mathcal{Y}(R)$  have been defined earlier. The energies for all the rovibrational states of  $\text{H}_2$ ,  $\text{D}_2$  and  $\text{T}_2$  are given in Ref. [40], whereas for  $\text{HD}$  in Ref. [41]. Those works contain also all the information needed to perform calculations for the rest of the isotopomers, which is exploited in the later chapters of the thesis.

Despite being the most demanding nonrelativistic contribution covered by the thesis, there is not much more to say about it here – it has already been described in detail during the presentation of the NAPT formalism. However, this is a good point at which to recapitulate the fully nonadiabatic approach because it entails all the described contributions originating from the moving nuclei, as well as all the others higher in  $m/\mu_n$  (the whole first column in Figure 3.1). Thus the most accurate nonrelativistic results are calculated in that regime [45, 17]. Nevertheless, as will be covered in Chapter 6, Eq. (3.34) is amazingly useful for rapid evaluation of the nonrelativistic energy should the



fully nonadiabatic result be unavailable. This is because it can generate all the rovibrational energies for all the H<sub>2</sub> isotopomers once  $\mu_{\parallel}(R)$ ,  $\mu_{\perp}(R)$ ,  $\mathcal{W}_{\parallel}(R)$  and  $\mathcal{Y}(R)$  for an electronic state  $|\psi\rangle$  are given.

### Relativistic BO contribution $E^{(4,0)}$

The leading relativistic Born-Oppenheimer contribution is defined by

$$H^{(4,0)} = -\frac{p_1^4 + p_2^4}{8} - \frac{1}{2}p_1^i \left( \frac{\delta^{ij}}{r_{12}} + \frac{r_{12}^i r_{12}^j}{r_{12}^3} \right) p_2^j + \pi \delta^3(r_{12}) + \frac{\pi}{2} (\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})), \quad (3.51)$$

$$\mathcal{E}^{(4,0)}(R) = \langle \psi | H^{(4,0)} | \psi \rangle, \quad (3.52)$$

$$E^{(4,0)} = \langle \chi | \mathcal{E}^{(4,0)}(R) | \chi \rangle. \quad (3.53)$$

Note that, compared to Eq. (2.16), some terms have been dropped in the Breit-Pauli Hamiltonian. Apart from the kinetic energy and contact terms for nuclei – whose absence is rather obvious – also the Breit nucleus-electron and nucleus-nucleus terms have been neglected. All of them are of higher orders in  $m/\mu_n$  and do not contribute here. This correction was taken into account as early as in the works of Kołos and Wolniewicz [9], but only recently was it recalculated with accuracy sufficient to prevent it from contributing significantly to the total uncertainty [23].

As a side note – literally speaking, the Born-Oppenheimer approximation refers to the approximate factorisation of the (nonrelativistic) Schrödinger equation only. In the thesis, however, all the NRQED/NAPT contributions of the zeroth order in  $m/\mu_n$  are called ‘BO’ – in analogy to the  $E^{(2,0)}$  being of this order, and to stress that the total energy is calculated with the BO nuclear function  $\chi(R)$  (3.44).

### Relativistic nonadiabatic contribution $E^{(4,1)}$

The main topic of the thesis. Two (of three) terms of the relativistic nonadiabatic contribution can be obtained simply by inserting the relativistically-corrected wave function into the formula for the adiabatic correction (3.21)

$$\begin{aligned} \langle \psi + \psi_{\text{rel}} | H_n | \psi + \psi_{\text{rel}} \rangle &= \langle \psi | H_n | \psi \rangle + \langle \psi_{\text{rel}} | H_n | \psi_{\text{rel}} \rangle + \frac{1}{\mu_n} \langle \vec{\nabla}_R \psi_{\text{rel}} | \vec{\nabla}_R \psi \rangle - \frac{1}{\mu_n} \langle \psi_{\text{rel}} | \vec{\nabla}_{\text{el}}^2 | \psi \rangle \\ &= \mathcal{E}^{(2,1)}(R) + \mathcal{E}_1^{(6,1)}(R) + \frac{1}{\mu_n} \mathcal{E}_1^{(4,1)}(R) + \frac{1}{\mu_n} \mathcal{E}_2^{(4,1)}(R), \end{aligned} \quad (3.54)$$

where

$$|\psi_{\text{rel}}\rangle = \frac{1}{(\mathcal{E} - H)'} H^{(4,0)} |\psi\rangle, \quad (3.55)$$

$$\mathcal{E}^{(2,1)}(R) = \langle \psi | H_n | \psi \rangle, \quad (3.56)$$

$$\mathcal{E}_1^{(6,1)}(R) = \langle \psi_{\text{rel}} | H_n | \psi_{\text{rel}} \rangle, \quad (3.57)$$

and where

$$\mathcal{E}_1^{(4,1)}(R) = \langle \vec{\nabla}_R \psi_{\text{rel}} | \vec{\nabla}_R \psi \rangle, \quad (3.58)$$

$$\mathcal{E}_2^{(4,1)}(R) = - \langle \psi_{\text{rel}} | \vec{\nabla}_{\text{el}}^2 | \psi \rangle. \quad (3.59)$$

$\mathcal{E}^{(2,1)}(R)$  can be recognised as the (nonrelativistic) adiabatic correction (3.21), and  $\mathcal{E}_1^{(6,1)}(R)$  is a term contributing in a higher order of  $\alpha$ . We are interested here in the relativistic nonadiabatic correction  $\mathcal{E}^{(4,1)}(R)$  – so we keep  $\mathcal{E}_1^{(4,1)}(R)$  and  $\mathcal{E}_2^{(4,1)}(R)$  only. One could point out that the function  $|\psi + \psi_{\text{rel}}\rangle$  used above is not normalised

$$\langle \psi + \psi_{\text{rel}} | \psi + \psi_{\text{rel}} \rangle = \langle \psi | \psi \rangle + \langle \psi_{\text{rel}} | \psi_{\text{rel}} \rangle = 1 + \langle \psi_{\text{rel}} | \psi_{\text{rel}} \rangle \quad (3.60)$$

Fortunately, the second, potentially problematic term is of the  $\alpha^6 m$  order<sup>4</sup>, which is irrelevant here.

As mentioned, these are not all the terms contributing in this order.

$$\mathcal{E}_3^{(4,1)}(R) = \mu_n \langle \psi | H_M^{(4,1)} | \psi \rangle, \quad (3.61)$$

$$H_M^{(4,1)} = - \sum_{a=1,2} \sum_{N=A,B} \frac{1}{2M_N} \nabla_a^i \left( \frac{\delta^{ij}}{r_{aN}} + \frac{r_{aN}^i r_{aN}^j}{r_{aN}^3} \right) \nabla_N^j. \quad (3.62)$$

This term can be easily recognised as the sum of the electron-nucleus Breit terms that were ‘missing’ in the  $H^{(4,0)}$  (3.51) and resurface here, in this NAPT order. We keep the coordinate system introduced in Chapter 2 – with the origin at the geometric centre of the nuclei, so  $H_M^{(4,1)}$  takes the form

$$\begin{aligned} H_M^{(4,1)} = & - \frac{1}{4\mu_n} \sum_{a=1,2} \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \nabla_R^j \\ & + \frac{1}{4\mu_n} \sum_{a=1,2} \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} + \frac{\delta^{ij}}{r_{aB}} + \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \nabla_{\text{el}}^j. \end{aligned} \quad (3.63)$$

Thus, a combined, nonadiabatic relativistic (electronic) correction  $\mathcal{E}^{(4,1)}(R)$  can be represented as the sum of three terms

$$\mathcal{E}^{(4,1)}(R) = \frac{1}{\mu_n} \left[ \mathcal{E}_1^{(4,1)}(R) + \mathcal{E}_2^{(4,1)}(R) + \mathcal{E}_3^{(4,1)}(R) \right], \quad (3.64)$$

which are defined above. The explicit formulas for  $\mathcal{E}^{(4,1)}$  will be derived in the next chapter. The total energy contribution of this order is as follows

$$E^{(4,1)} = \langle \chi | \mathcal{E}^{(4,1)}(R) | \chi \rangle + 2 \langle \chi | \delta \chi \rangle, \quad (3.65)$$

<sup>4</sup>In the context it is used, it would generate a term of the  $\alpha^6 m \cdot m / \mu_n$  order, the same as the neglected  $\mathcal{E}_1^{(6,1)}(R)$ .

$$|\delta\chi\rangle = \mathcal{E}^{(4,0)}(R) \frac{1}{(E^{(2,0)} - H_N)} \mathcal{E}^{(2,1)}(R) |\chi\rangle. \quad (3.66)$$

The additional term above is a second-order mixed relativistic/adiabatic correction.

The nonadiabatic relativistic contribution has been mistakenly neglected for a long time, due to fortuitous errors in the previous calculations of the relativistic BO correction  $E^{(4,0)}$  [25]. When  $E^{(4,0)}$  has been recalculated in Ref. [23] with a more reliable and accurate method, it exposed an experimental-theoretical discrepancy. The missing nonadiabatic relativistic correction  $E^{(4,1)}$  was its most probable source. It was proven to be true in Refs [36, 46] – where the relativistic contribution was treated in the fully nonadiabatic approach, as well as in Ref. [47] – where it was calculated directly.

### Leading QED BO contribution $E^{(5,0)}$

The leading QED Born-Oppenheimer contribution can be expressed as [27, 21, 48, 49]

$$E^{(5,0)} = \langle\chi|\mathcal{E}^{(5,0)}(R)|\chi\rangle, \quad (3.67)$$

where

$$\begin{aligned} \mathcal{E}^{(5,0)}(R) = & \frac{4}{3} \left[ \frac{19}{30} - 2 \ln \alpha - \ln k_0(R) \right] \sum_{a,X} \langle\psi|\delta^3(r_{aX})|\psi\rangle \\ & + \left[ \frac{164}{15} + \frac{14}{3} \ln \alpha \right] \langle\psi|\delta^3(r_{12})|\psi\rangle - \frac{7}{6\pi} \langle\psi|P\left(\frac{1}{r_{12}^3}\right)|\psi\rangle, \end{aligned} \quad (3.68)$$

and where:  $\ln k_0(R)$  – (electronic) Bethe logarithm and  $\langle\psi|P\left(\frac{1}{r_{12}^3}\right)|\psi\rangle$  – Araki-Sucher term. The Araki-Sucher term is defined as the following distribution

$$\langle\psi|P\left(\frac{1}{r_{12}^3}\right)|\psi\rangle = \lim_{a \rightarrow 0} \left[ \langle\psi|\frac{\theta(r_{12} - a)}{r_{12}^3}|\psi\rangle + 4\pi(\gamma_E + \ln a) \langle\psi|\delta^3(r_{12})|\psi\rangle \right], \quad (3.69)$$

with  $\theta$  being a Heaviside step function and  $\gamma_E$  – Euler-Mascheroni constant. The main difficulty in calculation of  $E^{(5,0)}$  is the notorious Bethe logarithm, defined as

$$\ln k_0(R) = \frac{\langle\psi|\vec{j}(H - \mathcal{E}) \ln[2(H - \mathcal{E})]\vec{j}|\psi\rangle}{\langle\psi|\vec{j}(H - \mathcal{E})\vec{j}|\psi\rangle}, \quad (3.70)$$

where

$$\vec{j} = -\frac{\vec{p}_1}{m} - \frac{\vec{p}_2}{m}. \quad (3.71)$$

The formula (3.70) involves a logarithm of the Hamiltonian, calculation of which requires very costly computation methods (see, for example, Ref. [24]). The  $E^{(5,0)}$  contribution for  $H_2$  was calculated in Ref. [21]. Note however, that it was calculated there with an adiabatically corrected nuclear function, which gives a slightly different result than in

the approach used in the thesis<sup>5</sup>. The results for the Araki-Sucher term and Dirac  $\delta$  have since been improved [23, 22]. It is also worth mentioning that recently the leading QED contribution was calculated very accurately for the ground state of  $\text{H}_2$  in the fully nonadiabatic regime [24]. It not only allowed the magnitude of the nonadiabatic QED effects to be observed, but also – as an added benefit – the accuracy of the previous Bethe logarithm calculations [21] to be corroborated. Currently, neglect of the nonadiabatic QED  $E^{(5,1)}$  effects is considered the main source of the theoretical uncertainty for the energy levels in hydrogen molecule.

### High-order QED (HQED) BO contributions $E^{(6,0)}$ , $E^{(7,0)}$

From this point on, the expressions for NRQED corrections become challengingly complex to derive. In the  $\alpha^6 m$  order, there are two contributions

$$\mathcal{E}^{(6,0)}(R) = \langle \psi | H^{(6,0)} | \psi \rangle + \langle \psi | H^{(4,0)} \frac{1}{(\mathcal{E} - H)'} H^{(4,0)} | \psi \rangle. \quad (3.72)$$

The latter one is just the second-order correction with respect to the Breit-Pauli Hamiltonian.  $H^{(4,0)}$  contains Dirac  $\delta$  and  $p^4$  operators, which are known to be divergent if used as a perturbation beyond the first order. Interestingly enough, the other term,  $\langle \psi | H^{(6,0)} | \psi \rangle$ , is divergent too – and these divergences cancel out when summed [22]. To handle this cancellation properly, dimensional regularisation is used [50]. The explicit formulas for  $\mathcal{E}^{(6,0)}(R)$  are extensive and well beyond the scope of this thesis. They can be found in Ref. [22]. The total energy contribution of this order is the following

$$E^{(6,0)} = \langle \chi | \mathcal{E}^{(6,0)}(R) | \chi \rangle + \langle \chi | \mathcal{E}^{(4,0)}(R) \frac{1}{(E^{(2,0)} - H_N)'} \mathcal{E}^{(4,0)}(R) | \chi \rangle. \quad (3.73)$$

The second term in the above equation is the second-order correction with respect to the relativistic BO potential. Thus, in the literature it is sometimes included in the  $E^{(4)}$  correction (e.g. in Ref. [23]) or shown explicitly [47]. In the thesis,  $E^{(n,k)}$  denotes the total correction of the order  $\alpha^n m \cdot (m/\mu_n)^k$ , so that term is included in  $E^{(6,0)}$ , and – consequently – in  $E^{(6)}$ .

The formulas for the  $\alpha^7 m$  contribution are not yet fully known for the hydrogen molecule – or even for the helium atom for that matter. Their estimate used at the current level of theory is based on the leading term for atomic hydrogen [24]

$$\begin{aligned} H^{(7,0)} &\approx \pi \left\langle \sum_{a,x} \delta^3(r_{ax}) \right\rangle \left\{ \frac{1}{\pi} [A_{60} + A_{61} \ln \alpha^{-2} + A_{62} \ln^2 \alpha^{-2}] + \frac{1}{\pi^2} B_{50} + \frac{1}{\pi^3} C_{40} \right\} \\ &\approx -0.858549 [\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})] \ln^2(\alpha^{-2}), \end{aligned} \quad (3.74)$$

where the coefficients used above are presented in the Table 3.1. With that said, the

<sup>5</sup>It was contaminated by some higher-order  $(m/\mu_n)^n$  contributions, so it was not  $E^{(5,0)}$  as defined in this thesis – see the argumentation for  $E^{(2,1)}$ . However, that work provided all the potentials we need to calculate it.

Table 3.1: Values of the coefficients in Eq. (3.74).  $A_{60}$  and  $A_{61}$  contain the vacuum-polarisation contribution.

Coefficient	Value	References
$A_{60}$	$-31.50104159(1)$	[52]
$A_{61}$	$5.28604$	[51]
$A_{62}$	$-1$	[51]
$B_{50}$	$-21.554449(13)$	[52]
$C_{40}$	$0.417504$	[51]

(approximate) energy contribution of this order is simply

$$\mathcal{E}^{(7,0)}(R) = \langle \psi | H^{(7,0)} | \psi \rangle, \quad (3.75)$$

$$E^{(7,0)} = \langle \chi | \mathcal{E}^{(7,0)}(R) | \chi \rangle. \quad (3.76)$$

When the currently leading error contributor ( $E^{(5,1)}$ ) is calculated,  $E^{(7,0)}$  will become the next step for improvement of the theory. Regarding its complexity, it is truly a long-term endeavour.

### Finite nucleus size correction $E_{\text{FS}}$

In order to obtain the level of accuracy we aim to achieve, we must take into account that the nuclei are not point-like particles. Such correction due to the finite nuclear size can be expressed as [51]

$$E_{\text{FS}} = \langle \chi | \mathcal{E}_{\text{FS}}(R) | \chi \rangle, \quad (3.77)$$

$$\mathcal{E}_{\text{FS}}(R) = \langle \psi | H_{\text{FS}} | \psi \rangle, \quad (3.78)$$

where

$$H_{\text{FS}} = \frac{2\pi}{3} [\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})] \frac{(r_A^2 + r_B^2)}{2}, \quad (3.79)$$

and where  $r_{A/B}$  is the root mean square charge radius of the  $A/B$  nucleus. Any higher-order effects due to nuclear size or nuclear polarisability are negligible at the current accuracy level – which is deduced from atomic hydrogen and deuterium [51]. Due to the Dirac  $\delta$ s being calculated for  $E^{(4,0)}$  anyway, the finite nucleus size correction (as well as the approximated  $E^{(7,0)}$ ) can be obtained virtually effortlessly. Note that its accuracy is limited by the accuracy of charge radii  $r_{A/B}$ , which is particularly evident in the tritium case (see Table 6.1 in the further part of the thesis). Conversely, it is  $E_{\text{FS}}$  which allows us to tie the dissociation energy of  $\text{H}_2$  to the proton charge radius and potentially use Eq. (1.1) to determine it.



## Relativistic nonadiabatic corrections

The key points of the derivations presented in this chapter have been published in our paper [47]. Since this NRQED/NAPT contribution is the main topic of my thesis, I would like to present it here in a greater detail. As covered in the previous chapter, the relativistic nonadiabatic correction can be expressed as the sum of three terms (3.64), which are gathered below

$$\mathcal{E}^{(4,1)}(R) = \frac{1}{\mu_n} \left[ \mathcal{E}_1^{(4,1)}(R) + \mathcal{E}_2^{(4,1)}(R) + \mathcal{E}_3^{(4,1)}(R) \right], \quad (4.1)$$

where (3.58, 3.59, 3.61)

$$\mathcal{E}_1^{(4,1)}(R) = \langle \vec{\nabla}_R \psi_{\text{rel}} | \vec{\nabla}_R \psi \rangle, \quad (4.2)$$

$$\mathcal{E}_2^{(4,1)}(R) = -\langle \psi_{\text{rel}} | \vec{\nabla}_{\text{el}}^2 | \psi \rangle, \quad (4.3)$$

$$\mathcal{E}_3^{(4,1)}(R) = \mu_n \langle \psi | H_M^{(4,1)} | \psi \rangle, \quad (4.4)$$

$$(4.5)$$

and where (3.55, 3.63)

$$|\psi_{\text{rel}}\rangle = \frac{1}{(\mathcal{E} - H)'} H^{(4,0)} |\psi\rangle, \quad (4.6)$$

$$\begin{aligned} H_M^{(4,1)} = & -\frac{1}{4\mu_n} \sum_{a=1,2} \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \nabla_R^j \\ & + \frac{1}{4\mu_n} \sum_{a=1,2} \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} + \frac{\delta^{ij}}{r_{aB}} + \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \nabla_{\text{el}}^j. \end{aligned} \quad (4.7)$$

There are several problems involved in these expressions. First of all, the potentials  $\mathcal{E}_1^{(4,1)}$  and  $\mathcal{E}_3^{(4,1)}$  contain  $\vec{\nabla}_R$  – a gradient with respect to the internuclear vector  $\vec{R}$ . When

we made the adiabatic approximation to the wave function, we obtained the electronic function  $|\psi\rangle$  which is not explicitly dependent on  $\vec{R}$ . However, it still depends on  $\vec{R}$  implicitly – through the electronic Schrödinger equation (3.11), which is solved for a *fixed value* of  $R$  – making the evaluation of  $\vec{\nabla}_R |\psi\rangle$  nontrivial. Secondly,  $H^{(4,0)}$  contains singular operators  $-p^4$  and Dirac  $\delta$ , which are difficult to handle in numerical calculations with Gaussian basis sets. Let us tackle these problems one by one.

## 4.1 Nuclear gradients

As mentioned, the electronic wave function depends on  $R$  implicitly via Eq. (3.11). Thus, exploiting that connection, one can write

$$\vec{\nabla}_R(H - \mathcal{E})|\psi\rangle = 0, \quad (4.8)$$

$$\begin{aligned} \vec{\nabla}_R |\psi\rangle &= \frac{1}{(\mathcal{E} - H)'} \vec{\nabla}_R(V - \mathcal{E})|\psi\rangle + c|\psi\rangle \\ &= \frac{1}{(\mathcal{E} - H)'} \vec{\nabla}_R(V)|\psi\rangle, \end{aligned} \quad (4.9)$$

where  $c$  is a constant. Neither  $\vec{\nabla}_R(\mathcal{E})|\psi\rangle$  nor  $c|\psi\rangle$  contribute in Eq. (4.9) – the former due to orthogonality (see Eq. (3.17)), and the latter because  $c = \langle\psi|\vec{\nabla}_R|\psi\rangle = 0$ . The reduced resolvent above can be understood as a weighted projection on all the electronic ‘intermediate’ states  $|\psi_i\rangle$

$$\frac{1}{(\mathcal{E} - H)'} = \sum_i' \frac{|\psi_i\rangle\langle\psi_i|}{\mathcal{E} - \mathcal{E}_i}. \quad (4.10)$$

The primed sum means that the reference state  $|\psi\rangle$  in the summation above is omitted (confer Eq. (3.17)). In practical implementation, a basis to represent such states has to be optimised. Thus, it is useful to split  $\vec{\nabla}_R |\psi\rangle$  into parts parallel and perpendicular to  $\vec{n}$

$$\vec{\nabla}_R |\psi\rangle = \vec{n} |\psi_a\rangle - \vec{n} \times |\vec{\psi}_a\rangle, \quad (4.11)$$

where

$$|\psi_a\rangle = \vec{n} \cdot \vec{\nabla}_R |\psi\rangle = \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V)|\psi\rangle, \quad (4.12)$$

$$|\vec{\psi}_a\rangle = \vec{n} \times \vec{\nabla}_R |\psi\rangle = \frac{1_{\Pi}}{(\mathcal{E} - H)'} \vec{n} \times \vec{\nabla}_R(V)|\psi\rangle, \quad (4.13)$$

and where  $\vec{n} = \vec{R}/R$ , and  $\vec{\nabla}_R(V)$  has already appeared in Chapter 3 during the description of the NAPT formalism (3.41), but is shown here again for convenience

$$\vec{\nabla}_R(V) = \frac{1}{2} \left( -\frac{\vec{r}_{1A}}{r_{1A}^3} + \frac{\vec{r}_{1B}}{r_{1B}^3} - \frac{\vec{r}_{2A}}{r_{2A}^3} + \frac{\vec{r}_{2B}}{r_{2B}^3} \right) - \frac{\vec{R}}{R^3}. \quad (4.14)$$



Such partition allows restriction of the summation in Eq. (4.10) and, in turn, of the basis set, to either  $\Sigma^+$  or  $\Pi$  functions only. The other type of functions will not contribute in the  $1/(\mathcal{E} - H)'$  summations due to symmetry.

Unfortunately, in the case of  $\vec{\nabla}_R |\psi_{\text{rel}}\rangle$  in  $\mathcal{E}_1^{(4,1)}$ , there is no such simple ‘trick’ as in Eq. (4.9). The dependence of  $|\psi_{\text{rel}}\rangle$  (3.55) on  $R$  is just too complicated. It is preferable to resort to numerical integration here. Obviously, it introduces a new source of uncertainty, but it is still a better solution than direct evaluation of  $\vec{\nabla}_R |\psi_{\text{rel}}\rangle$ . To achieve a numerically-integrable form, we can reform Eq. (4.2) into

$$\mathcal{E}_1^{(4,1)}(R) = \vec{\nabla}_R \langle \psi_{\text{rel}} | \vec{\nabla}_R \psi \rangle - \langle \psi_{\text{rel}} | \vec{\nabla}_R^2 \psi \rangle. \quad (4.15)$$

The first term above is the one evaluated by numerical differentiation

$$\begin{aligned} \vec{\nabla}_R \langle \psi_{\text{rel}} | \vec{\nabla}_R \psi \rangle &= \vec{\nabla}_R \cdot \vec{n} \langle \psi_{\text{rel}} | \vec{n} \cdot \vec{\nabla}_R \psi \rangle \\ &= \vec{\nabla}_R \cdot \left( \frac{\vec{R}}{R} \langle \psi_{\text{rel}} | \psi_a \rangle \right) = \vec{\nabla}_R \cdot \left( \frac{\vec{R}}{R^3} R^2 \langle \psi_{\text{rel}} | \psi_a \rangle \right) \\ &= \frac{\vec{R}}{R^3} \cdot \vec{\nabla}_R (R^2 \langle \psi_{\text{rel}} | \psi_a \rangle) = \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \langle \psi_{\text{rel}} | \psi_a \rangle). \end{aligned} \quad (4.16)$$

The numerical integration itself can be done by polynomial interpolation of  $\langle \psi_{\text{rel}} | \psi_a \rangle$  and subsequent differentiation of the polynomial found. After testing numerous interpolation schemes, the interpolation with splines of the fourth order was performed<sup>1</sup>. Furthermore, for the expression under the derivative a limit can be found analytically:  $\lim_{R \rightarrow 0} \langle \psi_{\text{rel}} | \psi_a \rangle = 0$ , so an additional point, stabilising the interpolation, could be added<sup>2</sup>.

The second term in Eq. (4.15) is transformed analogously to  $\vec{\nabla}_R |\psi\rangle$

$$\vec{\nabla}_R^2 |\psi\rangle = |\psi_{\text{na}}\rangle + c |\psi\rangle, \quad (4.17)$$

where

$$|\psi_{\text{na}}\rangle = \frac{1}{(\mathcal{E} - H)'} \left[ \vec{\nabla}_R^2(V) |\psi\rangle + 2 \vec{\nabla}_R(V - \mathcal{E}) \frac{1}{(\mathcal{E} - H)'} \vec{\nabla}_R(V) |\psi\rangle \right], \quad (4.18)$$

and where

$$\vec{\nabla}_R^2(V) = \pi [\delta^3(r_{1A}) + \delta^3(r_{2A}) + \delta^3(r_{1B}) + \delta^3(r_{2B})], \quad (4.19)$$

$$\vec{\nabla}_R(\mathcal{E}) = \vec{\nabla}_R(\langle \psi | H | \psi \rangle) = \langle \psi | \vec{\nabla}_R(V) | \psi \rangle. \quad (4.20)$$

Note that – contrary to Eq. (4.9) –  $\vec{\nabla}_R(\mathcal{E})$  and  $c |\psi\rangle$  cannot be so trivially omitted here. In the final formulas, however, the term  $c |\psi\rangle$  appears only next to a reduced resolvent from  $|\psi_{\text{rel}}\rangle$  in Eq. (4.15), so  $c |\psi\rangle$  cannot contribute anyway.

<sup>1</sup>In the **Mathematica 11.3** program [53].

<sup>2</sup>It is due to  $\lim_{R \rightarrow 0} r_{aA} = r_{aB}$ , which leads to  $\vec{\nabla}_R(V)$  vanishing.

The second resolvent in Eq. (4.18) can be decomposed into  $\Sigma^+$  and  $\Pi$  parts – exactly as in (4.11), which simplifies the numerical implementation. Thus, the following form of Eq. (4.15) is obtained

$$\mathcal{E}_1^{(4,1)}(R) = \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \langle \psi_{\text{rel}} | \psi_{\text{a}} \rangle) - \langle \psi_{\text{rel}} | \psi_{\text{na}} \rangle, \quad (4.21)$$

where

$$|\psi_{\text{na}}\rangle = \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{\nabla}_R^2(V) |\psi\rangle + 2 \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V - \mathcal{E}) |\psi_{\text{a}}\rangle + 2 \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \times \vec{\nabla}_R(V) |\vec{\psi}_{\text{a}}\rangle. \quad (4.22)$$

Note that  $\mathcal{E}$  depends on  $R$  only (not on the orientation of  $\vec{R}$ ), so  $\vec{n} \times \vec{\nabla}_R(\mathcal{E}) = 0$ . The term  $\mathcal{E}_2^{(4,1)}$  does not need any further transformations, whereas  $\mathcal{E}_3^{(4,1)}$  can – again – be partitioned into  $\Sigma^+/\Pi$  contributions

$$\begin{aligned} \mathcal{E}_3^{(4,1)}(R) = & \frac{1}{4} \sum_{a=1,2} \left[ \langle \psi | \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} + \frac{\delta^{ij}}{r_{aB}} + \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \nabla_{\text{el}}^j | \psi \rangle \right. \\ & - \langle \psi | n^j \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) | \psi_{\text{a}} \rangle \\ & \left. - \langle \psi | \epsilon^{mkj} n^k \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) | \psi_{\text{a}}^m \rangle \right]. \quad (4.23) \end{aligned}$$

With the formulas above, the problem caused by  $\vec{\nabla}_R$  can be considered solved.

## 4.2 Regularisation

As signalled before, the Breit-Pauli Hamiltonian  $H^{(4,0)}$  contains operators whose expectation values have slow numerical convergence. It is particularly evident when using a Gaussian basis set, whose elements have improper behaviour at coalescence points. The idea is simple but very efficient – the problematic singular operators are recast in a new form, comprising better-behaving ones [54, 55, 23]. Not to break the line of thought, the detailed derivation is moved to Appendix A. Here, only the result is provided.

$$4\pi\delta^3(r_{1A}) = \frac{4}{r_{1A}} (\mathcal{E} - V) - \vec{p}_1 \frac{2}{r_{1A}} \vec{p}_1 - \vec{p}_2 \frac{2}{r_{1A}} \vec{p}_2 + \left\{ \frac{2}{r_{1A}}, H - \mathcal{E} \right\}, \quad (4.24)$$

$$4\pi\delta^3(r_{12}) = \frac{2}{r_{12}} (\mathcal{E} - V) - \vec{p}_1 \frac{1}{r_{12}} \vec{p}_1 - \vec{p}_2 \frac{1}{r_{12}} \vec{p}_2 + \left\{ \frac{1}{r_{12}}, H - \mathcal{E} \right\}, \quad (4.25)$$

$$p_1^4 + p_2^4 = 4(\mathcal{E} - V)^2 - 2p_1^2 p_2^2 + 4(H - \mathcal{E})^2 + 4\{\mathcal{E} - V, H - \mathcal{E}\}. \quad (4.26)$$

As investigated in Ref. [23], such transformations already provide a significant boost in terms of numerical convergence. However, there is still some room for improvement.

Should the  $p_1^2 p_2^2$  in the above expression act on a wave function that satisfies Kato's cusp condition (see Chapter 5), the arising  $\delta^3(r_{12})$  function cancels out *exactly* with that from the Darwin correction in Eq. (3.52), effectively removing one important source of numerical error [23]. The remainder is denoted by  $\tilde{p}_1^2 \tilde{p}_2^2$

$$p_1^2 p_2^2 |\psi\rangle = \tilde{p}_1^2 \tilde{p}_2^2 |\psi\rangle - 4\pi\delta^3(r_{12}) |\psi\rangle, \quad (4.27)$$

where  $|\psi\rangle$  is assumed here to satisfy the Kato's cusp condition.

Such a regularisation scheme has been already employed in calculations of the BO relativistic corrections [23]. The key difference is that now the Breit-Pauli Hamiltonian can act on a wave function other than the one of the reference state (confer Eqs (3.55, 4.10)). It means that the terms in the anticommutators cannot be neglected, as they were in Ref. [23].

After regularisation, the Breit-Pauli Hamiltonian can be expressed as

$$\begin{aligned} H^{(4,0)} &= \left[ H^{(4,0)} \right]_r + \{Q, H - \mathcal{E}\} - \frac{1}{2} (H - \mathcal{E})^2, \quad (4.28) \\ \left[ H^{(4,0)} \right]_r &= -\frac{1}{2} (\mathcal{E} - V) \left( \mathcal{E} - \frac{1}{R} - \frac{1}{r_{12}} \right) + \frac{1}{4} (\tilde{p}_1^2 \tilde{p}_2^2 + p_1 \tilde{V} p_1 + p_2 \tilde{V} p_2) \\ &\quad - \frac{1}{2} p_1^i \left( \frac{\delta^{ij}}{r_{12}} + \frac{r_{12}^i r_{12}^j}{r_{12}^3} \right) p_2^j, \quad (4.29) \end{aligned}$$

where

$$Q = -\frac{1}{2} (\mathcal{E} - V) - \frac{1}{4} \tilde{V}, \quad (4.30)$$

$$\tilde{V} = -\frac{1}{r_{1A}} - \frac{1}{r_{2A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2B}}. \quad (4.31)$$

The Dirac  $\delta$ s which appear in the expression for  $\vec{\nabla}_R^2(V)$  (4.19) can be regularised also with Eq. (4.24)

$$\vec{\nabla}_R^2(V) = \left[ \vec{\nabla}_R^2(V) \right]_r - \frac{1}{2} \{ \tilde{V}, H - \mathcal{E} \}, \quad (4.32)$$

$$\left[ \vec{\nabla}_R^2(V) \right]_r = -(\mathcal{E} - V) \tilde{V} + \frac{1}{2} p_1 \tilde{V} p_1 + \frac{1}{2} p_2 \tilde{V} p_2. \quad (4.33)$$

With these new formulas, Eqs (3.55, 4.22) can be updated as well

$$|\psi_{\text{rel}}\rangle = |\psi_{\text{rel},r}\rangle + (|\psi\rangle \langle \psi| - 1) Q |\psi\rangle, \quad (4.34)$$

$$|\psi_{\text{rel},r}\rangle = \frac{1}{(\mathcal{E} - H)'} \left[ H^{(4,0)} \right]_r |\psi\rangle, \quad (4.35)$$

and

$$|\psi_{\text{na}}\rangle = |\psi_{\text{na},1}\rangle + 2 |\psi_{\text{na},2}\rangle + 2 |\psi_{\text{na},3}\rangle + \frac{1}{2} (1 - |\psi\rangle \langle \psi|) \tilde{V} |\psi\rangle, \quad (4.36)$$

$$|\psi_{\text{na},1}\rangle = \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \left[ \vec{\nabla}_R^2(V) \right]_r |\psi\rangle, \quad (4.37)$$

$$|\psi_{\text{na},2}\rangle = \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V - \mathcal{E}) |\psi_a\rangle, \quad (4.38)$$

$$|\psi_{\text{na},3}\rangle = \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \times \vec{\nabla}_R(V) |\vec{\psi}_a\rangle. \quad (4.39)$$

The next step is derivation of elementary expressions – ready for direct implementation in a computer code.

### 4.3 Elementary expressions

So far, everything needed to calculate the relativistic nonadiabatic correction has been already cast in a regularised form. However, it is obviously much more convenient to manage such complex calculations, e.g. code and look for possible errors, if the formulas to implement are elementary. Because of that, the formulas for  $\mathcal{E}_1^{(4,1)}(R)$ ,  $\mathcal{E}_2^{(4,1)}(R)$ , and  $\mathcal{E}_3^{(4,1)}(R)$  are split down to the expressions presented in this section.

$$\mathcal{E}_1^{(4,1)} = \frac{1}{R^2} \frac{\partial}{\partial R} (R^2(Y_1 - X_1)) - \langle \psi_{\text{rel}} | \psi_{\text{na}} \rangle, \quad (4.40)$$

$$\mathcal{E}_2^{(4,1)} = -X_4 - V_1 V_4 + V_5, \quad (4.41)$$

$$\mathcal{E}_3^{(4,1)} = \frac{1}{4} (V_6 - X_5 - X_6), \quad (4.42)$$

where

$$\langle \psi_{\text{rel}} | \psi_{\text{na}} \rangle = Y_2 + 2Z_1 + 2Z_2 + \frac{1}{2}X_2 - X_3 - 2Y_3 - 2Y_4 - \frac{1}{2}V_3 + \frac{1}{2}V_1 V_2. \quad (4.43)$$

All the  $V_i$ ,  $X_i$ ,  $Y_i$ , and  $Z_i$  represent the elementary expressions mentioned – of the first, second, third, and fourth order<sup>3</sup>, respectively. They are defined below.

#### First order

$$V_1 = \langle \psi | Q | \psi \rangle \quad (4.44)$$

$$V_2 = \langle \psi | \tilde{V} | \psi \rangle \quad (4.45)$$

$$V_3 = \langle \psi | Q \tilde{V} | \psi \rangle \quad (4.46)$$

$$V_4 = \langle \psi | \vec{\nabla}_{\text{el}}^2 | \psi \rangle \quad (4.47)$$

$$V_5 = \langle \psi | Q \vec{\nabla}_{\text{el}}^2 | \psi \rangle \quad (4.48)$$

<sup>3</sup>With *order* understood here similarly to the Rayleigh-Schrödinger perturbation calculus (1 + the number of reduced resolvents).

$$V_6 = \sum_{a=1,2} \langle \psi | \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} + \frac{\delta^{ij}}{r_{aB}} + \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \nabla_{\text{el}}^j | \psi \rangle \quad (4.49)$$

$$V_7 = \langle \psi | \vec{n} \cdot \vec{\nabla}_R(V) | \psi \rangle \quad (4.50)$$

### Second order

$$X_1 = \langle \psi | Q | \psi_a \rangle = \langle \psi | Q \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V) | \psi \rangle \quad (4.51)$$

$$X_2 = \langle \psi_{\text{rel},r} | \tilde{V} | \psi \rangle = \langle \psi | \left[ H^{(4,0)} \right]_r \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \tilde{V} | \psi \rangle \quad (4.52)$$

$$X_3 = \langle \psi | Q | \psi_{\text{na},1} \rangle = \langle \psi | Q \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \left[ \vec{\nabla}_R^2(V) \right]_r | \psi \rangle \quad (4.53)$$

$$X_4 = \langle \psi_{\text{rel},r} | \vec{\nabla}_{\text{el}}^2 | \psi \rangle = \langle \psi | \left[ H^{(4,0)} \right]_r \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{\nabla}_{\text{el}}^2 | \psi \rangle \quad (4.54)$$

$$X_5 = \sum_{a=1,2} \langle \psi | n^j \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) | \psi_a \rangle \quad (4.55)$$

$$= \sum_{a=1,2} \langle \psi | n^j \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V) | \psi \rangle$$

$$X_6 = \sum_{a=1,2} \langle \psi | \epsilon^{mkj} n^k \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) | \psi_a^m \rangle \quad (4.56)$$

$$= \sum_{a=1,2} \langle \psi | \epsilon^{mkj} n^k \nabla_a^i \left( \frac{\delta^{ij}}{r_{aA}} + \frac{r_{aA}^i r_{aA}^j}{r_{aA}^3} - \frac{\delta^{ij}}{r_{aB}} - \frac{r_{aB}^i r_{aB}^j}{r_{aB}^3} \right) \frac{1_{\Pi}}{\mathcal{E} - H} (\vec{n} \times \vec{\nabla}_R(V))^m | \psi \rangle$$

### Third order

$$Y_1 = \langle \psi_{\text{rel},r} | \psi_a \rangle = \langle \psi | \left[ H^{(4,0)} \right]_r \left( \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \right)^2 \vec{n} \cdot \vec{\nabla}_R(V) | \psi \rangle \quad (4.57)$$

$$Y_2 = \langle \psi_{\text{rel},r} | \psi_{\text{na},1} \rangle = \langle \psi | \left[ H^{(4,0)} \right]_r \left( \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \right)^2 \left[ \vec{\nabla}_R^2(V) \right]_r | \psi \rangle \quad (4.58)$$

$$Y_3 = \langle \psi | Q | \psi_{\text{na},2} \rangle = \langle \psi | Q \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} (\vec{n} \cdot \vec{\nabla}_R(V) - V_7) \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V) | \psi \rangle \quad (4.59)$$

$$Y_4 = \langle \psi | Q | \psi_{\text{na},3} \rangle = \langle \psi | Q \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \times \vec{\nabla}_R(V) \frac{1_{\Pi}}{\mathcal{E} - H} \vec{n} \times \vec{\nabla}_R(V) | \psi \rangle \quad (4.60)$$

### Fourth order

$$Z_1 = \langle \psi_{\text{rel},r} | \psi_{\text{na},2} \rangle$$

$$= \langle \psi | \left[ H^{(4,0)} \right]_r \left( \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \right)^2 \left( \vec{n} \cdot \vec{\nabla}_R(V) - V_7 \right) \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R(V) | \psi \rangle \quad (4.61)$$

$$\begin{aligned} Z_2 &= \langle \psi_{\text{rel},r} | \psi_{\text{na},3} \rangle \\ &= \langle \psi | \left[ H^{(4,0)} \right]_r \left( \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \right)^2 \vec{n} \times \vec{\nabla}_R(V) \frac{1_{\Pi}}{\mathcal{E} - H} \vec{n} \times \vec{\nabla}_R(V) | \psi \rangle \end{aligned} \quad (4.62)$$

## 4.4 Large $R$ asymptotics

Previous knowledge of the asymptotic behaviour of the evaluated quantity can be priceless. In this particular problem, such information can be used to check the correctness of the potentials obtained. Large  $R$  asymptotics for the elementary expressions provided in the last section can be investigated utilising the polarisation approximation [32]. It assumes that for the infinite internuclear separation  $R$ , the hydrogen molecule wave function factorises into the product of two hydrogen atom wave functions.

$$|\psi\rangle = |\psi_H(r_{1A})\rangle |\psi_H(r_{2B})\rangle, \quad (4.63)$$

$$\hat{H} = \hat{H}_1 + \hat{H}_2 = -\frac{\Delta_1}{2} - \frac{1}{r_{1A}} - \frac{\Delta_2}{2} - \frac{1}{r_{2B}}, \quad (4.64)$$

$$|\psi_H(r_{iN})\rangle = \frac{1}{\sqrt{\pi}} e^{-r_{iN}}, \quad (4.65)$$

where  $|\psi_H(r_{iN})\rangle$  is the ground state hydrogen atom wave function. For the expectation values of the elementary operators in  $V_1$ – $V_7$ ,  $X_1$ ,  $X_5$ , and  $X_6$ , the operators were then expanded in  $1/R$  at 0, keeping only the leading term, and then integrated with the wave function (4.63). In contrast to the previous part of the chapter, in the polarisation approximation nuclear gradients  $\vec{\nabla}_R$  are much easier to handle than reduced resolvents, so the former were brought back with the help of Eq. (4.9) in  $X_1$ ,  $X_5$ , and  $X_6$ . In the rest of the cases, where such a transformation was impossible (e.g. the resolvent appeared from Eq. (3.55)), a differential equation had to be solved. Fortunately, in the leading term of the  $1/R$  expansion, all the elementary operators could be factorised into sums of one-electron operators, so the differential equations to be solved were ordinary. All the values provided below could be quickly calculated with simple `Mathematica` [53] scripts written by us for that purpose.

### First order

$$V_1(\infty) = -\frac{1}{2} \quad (4.66)$$

$$V_2(\infty) = -2 \quad (4.67)$$

$$V_3(\infty) = \frac{3}{2} \quad (4.68)$$

$$V_4(\infty) = -\frac{1}{2} \quad (4.69)$$

$$V_5(\infty) = \frac{1}{2} \quad (4.70)$$

$$V_6(\infty) = -2 \quad (4.71)$$

$$V_7(\infty) = 0 \quad (4.72)$$

### Second order

$$X_1(\infty) = 0 \quad (4.73)$$

$$X_2(\infty) = -\frac{1}{2} \quad (4.74)$$

$$X_3(\infty) = \frac{1}{2} \quad (4.75)$$

$$X_4(\infty) = -\frac{1}{4} \quad (4.76)$$

$$X_5(\infty) = \frac{2}{3} \quad (4.77)$$

$$X_6(\infty) = \frac{4}{3} \quad (4.78)$$

### Third order

$$Y_1(\infty) = 0 \quad (4.79)$$

$$Y_2(\infty) = \frac{3}{4} - \frac{\pi^2}{6} \quad (4.80)$$

$$Y_3(\infty) = -\frac{1}{12} \quad (4.81)$$

$$Y_4(\infty) = -\frac{1}{6} \quad (4.82)$$

### Fourth order

$$Z_1(\infty) = -\frac{1}{8} + \frac{\pi^2}{36} \quad (4.83)$$

$$Z_2(\infty) = -\frac{1}{4} + \frac{\pi^2}{18} \quad (4.84)$$

Combining these values, it is easy to find that the  $R \rightarrow \infty$  asymptotic value of the relativistic nonadiabatic correction,  $\mathcal{E}^{(4,1)}(\infty)$ , is equal to 0. Further (numerical) tests suggest that for large distances  $\mathcal{E}^{(4,1)}(R)$  behaves like  $1/R^4$ , as it can be expected from Refs [56, 57]. Due to the above elementary expressions having different asymptotic behaviours, a significant cancellation between them occurs – which, in turn, reduces the accuracy in the long-range part of the potential curve.





# Numerical solution of the electronic Schrödinger equation

An archetypical quantum-chemical ‘black box’ relies on various flavors of Gaussian basis functions. In majority of quantum chemistry, one-electron Gaussian functions are employed, which do not involve inter-electronic distances. Due to the Gaussian product rule [42, 58], they allow to run calculations for systems with a theoretically arbitrary number of atoms. In fact, they are used to describe as complex systems as proteins (e.g. [59]). When speaking of high-accuracy calculations such as the ones presented in the thesis, where electronic correlation is an important factor, exponentially correlated Gaussians (ECG) are a reasonable choice of a basis set. They are the basis type ultimately chosen to calculate the nonadiabatic relativistic [47], as well as the relativistic BO [23], and the HQED [22]<sup>1</sup> corrections.

Despite the popularity of Gaussian bases, they are not an obvious choice in our case. They do not have the analytical properties of the exact wave function, in particular for coalescence points – which is described in the next section. It is a potential major hindrance when dealing with effects highly dependent on the behaviour of the wave function in these points. Additionally, they do not decay exponentially, which leads to poor description of long-range interactions. This is why our group undertook a research also of the other basis types. Development of algorithms for explicitly correlated exponential (ECE) bases has constituted an important part of my PhD studies, so a significant portion of this chapter is devoted to their description. It is an obvious departure from the main topic of the thesis. Thus – without breaking the line of thought – a Reader particularly interested in the nonadiabatic relativistic correction is free to skip the next two sections, proceeding to the one about ECG bases, and return here later.

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<sup>1</sup>With some help from exponential bases for expectation values of certain operators.

## 5.1 Kato's condition and singular operators

The main argument for using exponential basis sets over Gaussians is the mathematical 'correctness' of the former – they decay exponentially and, perhaps even more importantly, have a 'cusp' in the coalescence points. This last quality is known as fulfillment of the Kato's condition [60], which can be defined as follows

$$\left. \frac{\partial \psi(r_{ij})}{\partial r_{ij}} \right|_{r_{ij}=0} = \mu_{ij} q_i q_j \psi(r_{ij}) \Big|_{r_{ij}=0}, \quad (5.1)$$

where  $\psi(r_{ij})$  is the wave function,  $r_{ij}$  is the distance between the  $i$ -th and  $j$ -th particle (an electron or a nucleus),  $\mu_{ij}$  is the reduced mass of these two particles, and  $q_i, q_j$  are their electric charges.

Note that Gaussian-type basis functions clearly do not fulfill the above condition. In the nonrelativistic calculations it is barely noticeable because the great efficiency of the integral algorithms allows us to optimise fairly big basis sets, which far outweighs the incorrect behaviour of a single basis function. The possible problem starts when calculating a matrix element of a singular operator, like Dirac  $\delta$ .

$$\langle \psi | \delta^3(r_{ij}) | \psi \rangle = |\psi(r_{ij})|^2 \Big|_{r_{ij}=0}. \quad (5.2)$$

Its expectation value depends on the value of the wave function in the coalescence point – where it has incorrect analytical properties. It is even worse if the operator probes not the value of the function, but rather its derivative<sup>2</sup> over  $r_{ij}$  – then no matter how big the basis is, the result is plainly wrong – equal to 0. Had it not been for the regularisation techniques, it should disqualify bases not fulfilling Kato's condition from any calculations involving such singular operators.

## 5.2 Explicitly correlated exponential basis sets

An explicitly correlated exponential basis (ECE) is, in fact, the most natural one to choose. Just taking note of the  $Ne^{-ar}$ -type wave function of a hydrogen-like atom and trying to generalise it will surely lead first to the notion of the exponentially correlated basis of the following form

$$\psi_i = e^{-t_i r_{12} - u_i (r_{1A} + r_{1B}) - w_i (r_{2A} + r_{2B}) - y_i (r_{1A} - r_{1B}) - x_i (r_{2A} - r_{2B})}, \quad (5.3)$$

where subscripts 1, 2 denote electrons, A, B – the nuclei, and  $t, u, w, y, x$  are variational parameters. The basis (5.3) can describe the behaviour of the wave function properly both at short and long interparticle ranges, which leads in turn to smaller basis sets needed for given accuracy, especially in the calculation of expectation values of singular

<sup>2</sup>For example the Dirac  $\delta$  derivative, which appears in some QED operators.

operators mentioned earlier. In fact, the regularisation scheme presented in the previous chapter – although still viable – may not be necessary to achieve acceptable convergence. With a proper choice of the variational parameters, both a single function and a basis as a whole can fulfill Kato’s condition (5.1). The main problem with basis sets such as (5.3) are integrals that appear during calculations, more precisely the scarcity of general and efficient algorithms to deal with them.

Before delving deeper into the topic, it is worth mentioning other types of exponential bases. Kołos-Wolniewicz (KW) basis sets are patterned after the canonical works of these two scientists (e.g. Ref. [9]), and even today they are a good choice for  $\text{H}_2$  calculations (e.g. [43]). They have the following form

$$\begin{aligned} \psi_i = & r_{12}^{n_0} (r_{1A} + r_{1B})^{n_1} (r_{2A} + r_{2B})^{n_2} (r_{1A} - r_{1B})^{n_3} (r_{2A} - r_{2B})^{n_4} \\ & \times e^{-u_i(r_{1A}+r_{1B})-w_i(r_{2A}+r_{2B})-y_i(r_{1A}-r_{1B})-x_i(r_{2A}-r_{2B})}. \end{aligned} \quad (5.4)$$

A single function of such type does not fulfill the cusp condition (5.1) exactly, but it can still be approximated well with a sufficiently large basis. Due to not having the interelectronic distance  $r_{12}$  in the exponent, they lead to simpler integration algorithms than ECE bases. KW bases, with their polynomial factors naturally able to reproduce nodes, are particularly well suited to describe electronically excited states [61]. There are different ‘flavors’ of KW functions, such as James-Coolidge (JC) or Heitler-London (HL) functions, which are better in the description of, respectively, short- and long-range interactions. A JC basis has  $x = y = 0$ , whereas in HL:  $x = u$ ,  $y = w$ . A huge (several tens of thousands of functions) fully nonadiabatic JC basis was used to obtain the current best estimation of the nonrelativistic energy [17]. All of the above: KW, JC, and HL, treat the electronic correlation polynomially only, trading some flexibility for easier and more efficient integration algorithms. This section of the thesis focuses on the fully exponential (ECE) bases (5.3). The formalism in the following sections was presented in detail in Refs [62, 63], and its implementation was my MSc project [64]. During my PhD studies, I improved the code – most notably by extending the algorithm for the cases when one of the variational parameters ( $t$ ) is close to 0 and embedding it in a parallel energy optimisation algorithm.

### Master integral

All integrals that appear when using the exponentially correlated basis in the Born-Oppenheimer regime can be represented with the ‘master integral’ shown below and its derivatives

$$f = R \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-tr_{12}-u(r_{1A}+r_{1B})-w(r_{2A}+r_{2B})-y(r_{1A}-r_{1B})-x(r_{2A}-r_{2B})}}{r_{1A}r_{1B}r_{2A}r_{2B}r_{12}}. \quad (5.5)$$

Obviously, for  $f$  to converge, the variational parameters cannot be completely arbitrary. From the behaviour of the master integral (5.5) when any of the electrons is placed

infinitely far from the rest of the particles, it can be deduced that the parametres have to obey

$$w > 0, \quad u > 0, \quad t > -2u \wedge t > -2w. \quad (5.6)$$

It is easy to see that variants of  $f$  with higher powers of  $r_{ij}$  (needed for evaluation of almost any operator emerging in the energy calculations) can be obtained by taking appropriate partial derivatives over  $t, u, w, x,$  and  $y$ :

$$f(n_0, n_1, n_2, n_3, n_4) \stackrel{def}{=} R \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-tr_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})}}{r_{1A} r_{1B} r_{2A} r_{2B} r_{12}} \\ \times (r_{12}^{n_0} (r_{1A} + r_{1B})^{n_1} (r_{2A} + r_{2B})^{n_2} (r_{1A} - r_{1B})^{n_3} (r_{2A} - r_{2B})^{n_4}), \quad (5.7)$$

$$f(n_0, n_1, n_2, n_3, n_4) = \left(-\frac{\partial}{\partial t}\right)^{n_0} \left(-\frac{\partial}{\partial u}\right)^{n_1} \left(-\frac{\partial}{\partial w}\right)^{n_2} \left(-\frac{\partial}{\partial y}\right)^{n_3} \left(-\frac{\partial}{\partial x}\right)^{n_4} f. \quad (5.8)$$

Of course

$$f(0, 0, 0, 0, 0) \stackrel{def}{=} f.$$

The nonrelativistic  $H_2$  Hamiltonian in the BO approximation can be expressed as [63]

$$\langle \psi_i | \psi_j \rangle = \frac{1}{16 R} [f(1, 2, 2, 0, 0) + f(1, 0, 0, 2, 2) - f(1, 0, 2, 2, 0) - f(1, 2, 0, 0, 2)], \quad (5.9)$$

$$\langle \psi_i | V | \psi_j \rangle = \frac{1}{16 R} [f(0, 2, 2, 0, 0) + f(0, 0, 0, 2, 2) - f(0, 0, 2, 2, 0) - f(0, 2, 0, 0, 2)] \\ + \frac{1}{4 R} [f(1, 0, 2, 1, 0) + f(1, 2, 0, 0, 1) - f(1, 0, 0, 1, 2) - f(1, 0, 0, 2, 1)] \\ + \frac{1}{16 R^2} [f(1, 2, 2, 0, 0) + f(1, 0, 0, 2, 2) - f(1, 0, 2, 2, 0) - f(1, 2, 0, 0, 2)], \quad (5.10)$$

$$\langle \psi_i | T | \psi_j \rangle = \left( 2(u_i^2 t_j - y_j^2 t_j + u_j^2 t_i - y_j^2 t_i) R^2 [f(1, 0, 0, 0, 2) - f(1, 0, 2, 0, 0)] \right. \\ + 2(w_i^2 t_j - x_j^2 t_j + w_j^2 t_i - x_j^2 t_i) R^2 [f(1, 0, 0, 2, 0) - f(1, 2, 0, 0, 0)] \\ + (2w_i^2 t_j + 2y_i^2 t_j + 2w_j^2 t_i + 2y_j^2 t_i - tt_j t_i) f(1, 2, 0, 0, 2) \\ + (2u_i^2 t_j + 2x_i^2 t_j + 2u_j^2 t_i + 2x_j^2 t_i - tt_j t_i) f(1, 0, 2, 2, 0) \\ - (2u_i^2 t_j + 2w_i^2 t_j + 2u_j^2 t_i + 2w_j^2 t_i - tt_j t_i) f(1, 0, 0, 2, 2) \\ - (2y_i^2 t_j + 2x_i^2 t_j + 2y_j^2 t_i + 2x_j^2 t_i - tt_j t_i) f(1, 2, 2, 0, 0) \\ + 4(u_i t_j + u_j t_i) [f(1, 0, 0, 1, 2) - f(1, 0, 2, 1, 0)] \\ + 4(w_i t_j + w_j t_i) [f(1, 0, 0, 2, 1) - f(1, 2, 0, 0, 1)] \\ + 4(y_i t_j + y_j t_i) [f(1, 1, 2, 0, 0) - f(1, 1, 0, 0, 2)] \\ \left. + 4(x_i t_j + x_j t_i) [f(1, 2, 1, 0, 0) - f(1, 0, 1, 2, 0)] \right) / (16 t R), \quad (5.11)$$

where  $t = t_i + t_j$  (this convention will be used further also for all the other variational parametres). The Hamiltonian matrix elements are thus finite combinations of derivatives

of the master integral, and the problem of energy calculation is reduced to the evaluation of them. Note the presence of one of the variational parameters ( $t$ ) in the denominator of the expression for the kinetic energy. For obvious reasons, it can be a problem for the generality of the algorithm. The consequences – and the way of dealing with them – will be covered further.

### Taylor series

The approach presented here stems from the concept originally proposed by Fromm and Hill for the lithium atom [65] – that the master integral can be represented as a series in the internuclear distance  $R$

$$f = \sum_{n=1}^{\infty} f_n R^n, \quad (5.12)$$

$$f_n = f_n^{(1)} \ln(R) + f_n^{(2)}. \quad (5.13)$$

This series is absolutely convergent for any value of  $R$  [65]. Fromm and Hill's way of obtaining expressions for  $f_n$  is not particularly convenient, however. A differential equation for  $f$  would be extremely helpful, so one could derive recurrence relations for the series coefficients. Luckily, it was shown by Pachucki in Ref. [62] that  $f$  satisfies the following equation

$$\left[ \sigma_4 \frac{d^2}{dR^2} R \frac{d^2}{dR^2} + \sigma_2 \frac{d}{dR} R \frac{d}{dR} + \sigma_0 R \right] f = F, \quad (5.14)$$

where

$$\begin{aligned} \sigma_4 &= t^2, \\ \sigma_2 &= t^4 - 2t^2(u^2 + w^2 + x^2 + y^2) + 16uwx y, \\ \sigma_0 &= t^2(u + w - x - y)(u - w + x - y)(u - w - x + y)(u + w + x + y) \\ &\quad + 16(w x - u y)(u x - w y)(u w - x y). \end{aligned} \quad (5.15)$$

$F$  is an inhomogeneous term of the following form [62]

$$\begin{aligned} F &= t \left( \frac{1}{R^2} + \frac{2t + u + w + x - y}{R} \right) e^{-R(u+w+t+x-y)} \\ &\quad + t \left( \frac{1}{R^2} + \frac{2t + u + w - x + y}{R} \right) e^{-R(u+w+t-x+y)} \\ &\quad - t \left( \frac{1}{R^2} + \frac{u + w - x - y}{R} \right) e^{-R(u+w-x-y)} \\ &\quad - t \left( \frac{1}{R^2} + \frac{u + w + x + y}{R} \right) e^{-R(u+w+x+y)} \end{aligned}$$

$$\begin{aligned}
 & + \left[ \frac{t^2}{2}(u - w + x - y) + 2u w(y - x) + 2x y(w - u) \right] F_1 \\
 & + \left[ \frac{t^2}{2}(u - w - x + y) + 2u w(x - y) + 2x y(w - u) \right] F_2 \\
 & + \left[ \frac{t^2}{2}(u + w + x + y) + 2u w(x + y) + 2x y(w + u) \right] F_3 \\
 & + \left[ \frac{t^2}{2}(u + w - x - y) - 2u w(x + y) + 2x y(w + u) \right] F_4, \tag{5.16}
 \end{aligned}$$

with

$$\begin{aligned}
 F_1 &= \text{Ei}[-R(t + 2u)]e^{R(u-w+x-y)} - \text{Ei}[-R(t + 2w)]e^{-R(u-w+x-y)}, \\
 F_2 &= \text{Ei}[-R(t + 2u)]e^{R(u-w-x+y)} - \text{Ei}[-R(t + 2w)]e^{-R(u-w-x+y)}, \\
 F_3 &= \text{Ei}[-2R(u + w)]e^{R(u+w+x+y)} + \left( \text{Ei}[2R(x + y)] - \text{Ei}[-R(t - 2x)] \right. \\
 & \quad \left. - \text{Ei}[-R(t - 2y)] - \ln \left| \frac{(t + 2u)(t + 2w)(x + y)}{(u + w)(t - 2x)(t - 2y)} \right| \right) e^{-R(u+w+x+y)}, \\
 F_4 &= \text{Ei}[-2R(u + w)]e^{R(u+w-x-y)} + \left( \text{Ei}[-2R(x + y)] - \text{Ei}[-R(t + 2x)] \right. \\
 & \quad \left. - \text{Ei}[-R(t + 2y)] - \ln \left| \frac{(t + 2u)(t + 2w)(x + y)}{(u + w)(t + 2x)(t + 2y)} \right| \right) e^{-R(u+w-x-y)}. \tag{5.17}
 \end{aligned}$$

$\text{Ei}(x)$  is an exponential integral defined as:

$$\text{Ei}(x) = - \int_{-x}^{\infty} \frac{e^{-t} dt}{t}. \tag{5.18}$$

Inserting Eq. (5.12) into Eq.(5.14) produces recurrence relations for  $f_n^{(1)}$  and  $f_n^{(2)}$  [62]:

$$f_n^{(1)} = \frac{F_{n-3}^{(1)} - \sigma_0 f_{n-4}^{(1)} - \sigma_2(n-2)^2 f_{n-2}^{(1)}}{\sigma_4 n(n-1)^2(n-2)}, \tag{5.19}$$

$$f_n^{(2)} = \frac{F_{n-3}^{(2)} - \sigma_0 f_{n-4}^{(2)} - \sigma_2(n-2)^2 f_{n-2}^{(2)} - 2\sigma_2(n-2) f_{n-2}^{(1)} - 2\sigma_4(n-1)(2n(n-2) + 1) f_n^{(1)}}{\sigma_4 n(n-1)^2(n-2)}, \tag{5.20}$$

where  $F_n^{(1)}$  and  $F_n^{(2)}$  are the terms of the Taylor expansion of the inhomogeneous term  $F$

$$F = \sum_{n=-1}^{\infty} \left[ F_n^{(1)} \ln(R) + F_n^{(2)} \right] R^n. \tag{5.21}$$

The formulas for  $F_n^{(1)}$  and  $F_n^{(2)}$ , as well as the leading recurrence terms, are provided in Appendix C. Please note that  $t$  again appears in the denominator of Eqs. (5.19, 5.20) (as  $\sigma_4 = t^2$ ).

The expressions for  $f(n_0, n_1, n_2, n_3, n_4)$  can be found either by explicit differentiation of the formulas shown above or by yet more recurrence relations<sup>3</sup>[63]. The recurrence relations can be faster, but they contain singularities limiting their applicability in certain ranges of the variational parameters. For example [63]

$$\frac{\partial f'(R)}{\partial x} = \frac{1}{t^2 - 4x^2} \left( -\frac{Rf(R)}{2} \frac{\partial \sigma_{02}}{\partial x} - 2Rx f''(R) + \frac{F_1 - F_2 + F_3 - F_4}{2} \right), \quad (5.22)$$

which prevents  $t \approx \pm 2x$  – putting additional restrictions on the variational space. In my work, I have followed the explicit differentiation, which is slower, but is the most general approach. In fact, probably the ideal solution is to use recurrences where possible and in the other cases fall back to the explicitly differentiated formulas.

### Small $t$ problem

As hinted before, the presence of  $t$ , one of the variational parameters, in the denominators of Eqs. (5.19, 5.20) does not bode well for the convergence of the above algorithm – it can be very slow for small  $t$ , and it completely fails for  $t = 0$ . Worse still, more significant digits cancel out in every iteration when  $t$  becomes small, and higher numerical precision is needed. An efficient numerical library (such as Ref. [66]) can be used to address that need, but it solves the problem only partially. For small enough  $t$ , series as long as several hundred terms can be reached, and there is still a problem when  $t = 0$ . In practice, it appears that such cases of dangerously small  $t$  are rare, happening only occasionally during basis set optimisation, but they should still be taken into account somehow. The most conceptually straightforward approach (taken here) is to expand Eqs. (5.19, 5.20, 5.16) not only in  $R$ , but also in  $t$ . It is a bit of a ‘brute force’ method (and its computational cost is high), but it is simple, and – because of the rarity of small  $t$  cases – it is sufficient

$$f = \sum_{n=1}^{\infty} \sum_{m=0}^{\infty} f_{nm} R^n t^m, \quad (5.23)$$

$$f_{nm} = f_{nm}^{(1)} \ln(R) + f_{nm}^{(2)}, \quad (5.24)$$

where

$$f_{nm}^{(1)} = \frac{F_{n-3,m+2}^{(1)} - \sigma_{40} f_{n-4,m}^{(1)} - \sigma_{42} f_{n-4,m+2}^{(1)} - (n-2)^2 (f_{n-2,m-2}^{(1)} + \sigma_{20} f_{n-2,m}^{(1)} + \sigma_{22} f_{n-2,m+2}^{(1)})}{n(n-1)^2(n-2)} \quad (5.25)$$

<sup>3</sup>Those connect  $f$  and its derivatives, rather than the expansion terms in  $R$ .

and

$$f_{nm}^{(2)} = \frac{F_{n-3,m+2}^{(2)} - \sigma_{40}f_{n-4,m}^{(2)} - \sigma_{42}f_{n-4,m+2}^{(2)} - (n-2)^2(f_{n-2,m-2}^{(2)} + \sigma_{20}f_{n-2,m}^{(2)} + \sigma_{22}f_{n-2,m+2}^{(2)})}{n(n-1)^2(n-2)} - \frac{2(n-1)(2n(n-2)+1)f_{nm}^{(1)} + 2(n-2)(f_{n-2,m-2}^{(1)} + \sigma_{20}f_{n-2,m}^{(1)} + \sigma_{22}f_{n-2,m+2}^{(1)})}{n(n-1)^2(n-2)}, \quad (5.26)$$

and where

$$\sigma_{20} = -2(u^2 + w^2 + x^2 + y^2), \quad (5.27)$$

$$\sigma_{22} = 16u \, w \, x \, y, \quad (5.28)$$

$$\sigma_{40} = (u + w - x - y)(u - w + x - y)(u - w - x + y)(u + w + x + y), \quad (5.29)$$

$$\sigma_{42} = 16(w \, x - u \, y)(u \, x - w \, y)(u \, w - x \, y). \quad (5.30)$$

Again, the explicit formulas for  $F_{nm}^{(1)}$  and  $F_{nm}^{(2)}$  – due to their length – are given in Appendix C, together with the starting recurrence terms.

In the case of expression (5.11) for the kinetic energy, the division by  $t$  is performed just once, so it has a very small impact on the numerical precision. Nevertheless, the problem when  $t = 0$  persists. In principle, the expectation value of the kinetic energy should not diverge when  $t \rightarrow 0$ , so this singularity has to be removable. It can be eliminated by extracting the problematic terms proportional to  $t^{-1}$  in Eq. (5.11) and omitting the first ( $t^0$ ) term in their Taylor expansion in  $t$ . The modified kinetic energy matrix element is the following

$$\begin{aligned} \langle \psi_i | T | \psi_j \rangle &= \frac{R}{16} \left( (u_i^2 + u_j^2 - y_i^2 - y_j^2)[f(1, 0, 0, 0, 2) - f(1, 0, 2, 0, 0)] \right. \\ &\quad \left. + (w_i^2 + w_j^2 - x_i^2 - x_j^2)[f(1, 0, 0, 2, 0) - f(1, 2, 0, 0, 0)] \right) \\ &\quad + \frac{1}{8R} \left( [f(1, 0, 0, 1, 2) - f(1, 0, 2, 1, 0)]u + [f(1, 0, 0, 2, 1) - f(1, 2, 0, 0, 1)]w \right. \\ &\quad \left. + [f(1, 2, 1, 0, 0) - f(1, 0, 1, 2, 0)]x + [f(1, 1, 2, 0, 0) - f(1, 1, 0, 0, 2)]y \right) \\ &\quad + \frac{1}{64R} \left( (-4(u_i^2 + u_j^2 + w_i^2 + w_j^2) + t^2 - (t_i - t_j)^2)f(1, 0, 0, 2, 2) \right. \\ &\quad + (4(u_i^2 + u_j^2 + x_i^2 + x_j^2) - t^2 + (t_i - t_j)^2)f(1, 0, 2, 2, 0) \\ &\quad + (4(w_i^2 + w_j^2 + y_i^2 + y_j^2) - t^2 + (t_i - t_j)^2)f(1, 2, 0, 0, 2) \\ &\quad \left. + (-4(y_i^2 + y_j^2 + x_i^2 + x_j^2) + t^2 - (t_i - t_j)^2)f(1, 2, 2, 0, 0) \right) \\ &\quad + \frac{t_i - t_j}{16R} \left( (u_i - u_j)(2[f'(1, 0, 2, 1, 0) - f'(1, 0, 0, 1, 2)] \right. \\ &\quad \left. + [f'(1, 0, 0, 2, 2) - f'(1, 0, 2, 2, 0) + R^2(f'(1, 0, 2, 0, 0) - f'(1, 0, 0, 0, 2))]u \right) \\ &\quad + (w_i - w_j)(2[f'(1, 2, 0, 0, 1) - f'(1, 0, 0, 2, 1)]) \end{aligned}$$



$$\begin{aligned}
& + [f'(1, 0, 0, 2, 2) - f'(1, 2, 0, 0, 2) + R^2(f'(1, 2, 0, 0, 0) - f'(1, 0, 0, 2, 0))]w \\
& + (x_i - x_j)(2[f'(1, 0, 1, 2, 0) - f'(1, 2, 1, 0, 0)] \\
& + [f'(1, 2, 2, 0, 0) - f'(1, 0, 2, 2, 0) + R^2(f'(1, 0, 0, 2, 0) - f'(1, 2, 0, 0, 0))]x \\
& + (y_i - y_j)(2[f'(1, 1, 0, 0, 2) - f'(1, 1, 2, 0, 0)] \\
& + [f'(1, 2, 2, 0, 0) - f'(1, 2, 0, 0, 2) + R^2(f'(1, 0, 0, 0, 2) - f'(1, 0, 2, 0, 0))]y).
\end{aligned} \tag{5.31}$$

In the formula above,  $f'$  denotes such an integral with a  $t^0$  term omitted.

### Convergence

With the size of a basis set increased, the maximal magnitude of the optimal variational parameters rises (Fig 5.1). It is an expected behaviour in variational calculations, be-

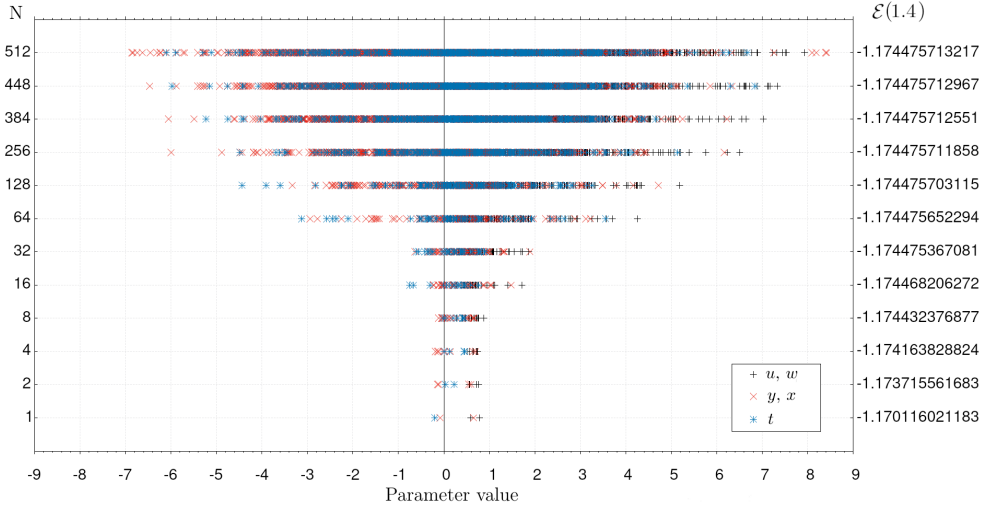


Figure 5.1: Value of the variational parameters  $t$ ,  $y$ ,  $x$ ,  $u$ ,  $w$  (after optimisation) for different basis set sizes  $N$ , with corresponding nonrelativistic BO energies  $\mathcal{E}(R)$  at the distance  $R = 1.4$  a.u.

cause adding new functions which are too similar to the ones existing in the basis does not improve the description of the system much. However, in the case of the presented algorithm, such an increase in the magnitude of the parameters has an especially significant efficiency impact. It can be illustrated by observing that the inhomogeneous term (5.16) contains terms of the  $e^{\pm\beta R}$  type, where  $\beta$  is some combination of the variational parameters. An expansion in  $R$  of the exponential function  $\frac{(|\beta_{\max}|R)^n}{n!}$  – where  $\beta_{\max}$  is the combination that has the biggest magnitude – turns out to be a good estimate of the magnitude of the terms of the recurrence series (5.12). When  $|\beta_{\max}|$  rises, the integer

$n$ , for which the terms become smaller than a convergence threshold assumed, obviously gets bigger too. Moreover, in Eq. (5.20) a significant numerical cancellation is observed in each recurrence step when any of the variational parameters  $u$ ,  $w$ ,  $x$ ,  $y$  becomes large<sup>4</sup>. These two effects combined can lead to the necessity of using very high starting numerical precision of the first recurrence terms. In the worst of cases, several-hundred-digit precision was required. Despite using an efficient arbitrary precision library [66] and heavy parallelisation, it is still time consuming.

It is worth noting that beyond nonrelativistic calculations one can encounter integrals with powers of distances lower than -1, and they cannot be generated with differentiation (5.8). Conversely, they require integration – for example [63]

$$\langle \psi | \frac{1}{r_{1A}^2} | \psi \rangle = \int_0^\infty dq \langle \psi | \frac{e^{-qr_{1A}}}{r_{1A}} | \psi \rangle. \quad (5.32)$$

It is not a problem itself – as the next chapter will cover, a similar phenomenon occurs also in ECG bases, and it can be resolved by using an efficient numerical quadrature, such as the one presented in Ref. [67]. The numerical integration can, however, require nodes that correspond to the master integral with one or more of the variational parameters assuming a large value<sup>5</sup>. As described above, for the ECE basis it poses a major efficiency problem. Potentially it can be solved via an (asymptotic) expansion of the master integral in  $q^{-1}$  rather than in  $R$ . It could automatically resolve not only the problem of the integrals with powers of distances lower than -1, but also improve the speed of the nonrelativistic calculations. Unfortunately, although Ref. [63] has shown how to construct such asymptotic series, in practice expressions only for its first few terms have been derived so far. It proved to be a limiting factor in using the method to calculate any of the NRQED/NAPT energy contributions described in Chapter 3.

The example of results of nonrelativistic energy calculations with ECE bases (5.3), compared to ECG (Gaussian) bases<sup>6</sup>, are presented in Table 5.1. It is noticeable that an exponential basis needs a significantly smaller number of functions to achieve much better accuracy – actually the 64-function ECE basis produces a better result than the 128-function ECG. However, for large sizes, the Gaussian bases start to outperform the exponential ones. A possible cause of such behaviour is the computational cost mentioned – the ECE basis of the size 512 could probably be optimised further, but it would still require a lot of time.

To sum up, the explicitly correlated exponential basis set is a viable choice in hydrogen energy calculations. However, to be competitive with KW and ECG bases, it requires further research – mainly constructing the asymptotic expansion for large variational parameters to increase its efficiency and to be able to tackle relativistic and QED problems.

<sup>4</sup>Or  $t$  becomes small, which has already been addressed with the  $t$  series expansion, but it still has some efficiency impact.

<sup>5</sup>In the example above:  $u \rightarrow u + q/2$ ,  $y \rightarrow y + q/2$ , and  $q$  can become large for some integration nodes.

<sup>6</sup>An ECG basis function differs from the ECE one (5.3) only by having the interparticle distances squared.

Table 5.1: Nonrelativistic energy  $\mathcal{E}(R)$  at the distance  $R = 1.4$  a.u., calculated with different basis set types.

$N$	ECE	ECG
64	-1.174 475 652 3	-1.174 473 672 8
128	-1.174 475 703 1	-1.174 475 623 4
256	-1.174 475 712 9	-1.174 475 711 7
512	-1.174 475 713 2	-1.174 475 714 1
$\infty$	-1.174 475 714 220 443 4(5) (JC, [18])	

An interesting alternative of alleviating the efficiency problem would be also to follow the pseudorandom approach (e.g. Ref. [68]). Rather than optimising the variational parameters for each basis function individually,  $t$ ,  $u$ ,  $w$ ,  $x$ ,  $y$  for a particular function are generated pseudorandomly. The ranges from which the parameters are picked are chosen variationally nonetheless – but there are still far fewer variables to optimise. This approach has been used for some time – with outstanding results – in calculations for the helium atom [69], where a similar (explicitly correlated exponential) basis was used.

### 5.3 Correlated Gaussian basis sets

Ultimately, the unfavourable computational cost scaling of the exponential functions, as well as the development of the regularisation techniques – which removed the biggest disadvantage of Gaussian bases, tipped the balance in favor of the latter. To calculate the nonadiabatic relativistic correction, explicitly correlated Gaussians (ECG) were used, which are very similar to the ECE basis functions covered in the previous section (5.3)

$$\phi_i = e^{-u_i r_{1A}^2 - w_i r_{1B}^2 - y_i r_{2A}^2 - x_i r_{2B}^2 - t_i r_{12}^2}. \quad (5.33)$$

The parameters  $u$ ,  $w$ ,  $y$ ,  $x$ ,  $t$  were optimised individually for each function. In addition – to be able to exploit identity (4.27) to eliminate the  $\delta^3(r_{12})$  term from the Breit-Pauli Hamiltonian, the so-called rECG functions were employed

$$\phi'_i = (1 + r_{12}/2) e^{-u_i r_{1A}^2 - w_i r_{1B}^2 - y_i r_{2A}^2 - x_i r_{2B}^2 - t_i r_{12}^2}, \quad (5.34)$$

which satisfy the inter-electronic cusp condition (5.1) exactly. Taking symmetry into account, the wave function was represented as the following linear combination

$$|\psi\rangle = (1 + \hat{i})(1 + P_{1\leftrightarrow 2}) \sum_i c_i \psi_i, \quad (5.35)$$

where  $\hat{i}$  is an inversion operator and  $P_{1\leftrightarrow 2}$  exchanges the electrons, and where

$$\psi_i = \begin{cases} \phi_i & \text{for } \Sigma^+ \text{ states,} \\ \vec{n} \times \vec{r}_{1A} \phi_i & \text{for } \Pi \text{ states.} \end{cases} \quad (5.36)$$

As previously,  $\vec{n} = \vec{R}/R$ . Both the kinds of Gaussian bases have been used before in Ref. [23].

The method of evaluation of the integrals that arise when an ECG basis is used, has been already described extensively, e.g. in Refs [23, 47]. As with the exponential basis covered in the previous section, all the matrix elements needed can be written down as linear combinations of some ‘master integral’  $f$  and its derivatives over the variational parametres

$$f(n_1, n_2, n_3, n_4, n_5) = \frac{1}{\pi^3} \int d^3 r_1 \int d^3 r_2 r_{1A}^{n_1} r_{1B}^{n_2} r_{2A}^{n_3} r_{2B}^{n_4} r_{12}^{n_5} \times e^{-u_i r_{1A}^2 - w_i r_{1B}^2 - y_i r_{2A}^2 - x_i r_{2B}^2 - t_i r_{12}^2}. \quad (5.37)$$

Here, however, unlike in the exponential case, differentiation raises  $n_i$  by multiplies of 2, so several master integrals are needed to calculate all the possible derivatives of  $f$ . The integrals with even powers of all the inter-particle distances can be obtained by differentiation of the following master integral [23]

$$f(0, 0, 0, 0, 0) = A^{-3/2} e^{-R^2 \frac{B}{A}}, \quad (5.38)$$

where

$$A = (u + w + t)(y + x + t) - t^2, \quad (5.39)$$

$$B = (w + u) y x + u w (y + x) + t (u + y)(w + x). \quad (5.40)$$

If one of the  $n_k$  indices is odd, the ECG integrals can also be obtained analytically by differentiation of other master integrals. As an example, the master integral for  $n_1 = -1$  is [23]

$$f(-1, 0, 0, 0, 0) = \frac{1}{A\sqrt{A_1}} e^{-R^2 \frac{B}{A}} F \left[ R^2 \left( \frac{B_1}{A_1} - \frac{B}{A} \right) \right], \quad (5.41)$$

where  $A_1 = \frac{\partial A}{\partial u}$ ,  $B_1 = \frac{\partial B}{\partial u}$ , and  $F(x) = \text{erf}(x)/x$ .

When two or more  $n_k$  indices are odd, there are no known analytic formulas for such an integral. In such situations, numerical integration can be used to lower one of the  $n_k$  powers by one, for example [23]

$$f(n_1 - 1, n_2, n_3, n_4, n_5) = \frac{2}{\sqrt{\pi}} \int_0^\infty dq f(n_1, n_2, n_3, n_4, n_5) \Big|_{u \rightarrow u+q^2}. \quad (5.42)$$

The one chosen by us, an extended Gaussian quadrature [67], is very similar to the ‘typical’ Gaussian quadratures, which are exact for a set of polynomials [70]. Here the set of  $2n$  functions, for which the quadrature is exact, is

$$\omega_i(x) = x^{i-1}, \quad (5.43)$$

$$\omega_{i+n}(x) = x^{i-1} \ln x. \quad (5.44)$$

Such quadrature retains the advantages of a Gauss-Legendre quadrature (fast convergence, simplicity), at the same time having an additional benefit of *much* better convergence if the integrand contains a logarithmic-type singularity (confer Ref. [67] for comparisons). In the scope of the thesis, the need for this kind of numerical integration does not arise during simple  $\mathcal{E}(R)$  energy evaluations. It is, however, necessary when dealing with relativistic effects – most notably in the elementary operators presented in Chapter 4 (4.44–4.62). Evaluation of  $V_3$  and  $X_3$  requires a single numerical integration, whereas evaluation of  $X_2$ ,  $X_4$ ,  $Y_1$ ,  $Y_2$ ,  $Z_1$ , and  $Z_2$  – containing integrals with three odd  $n_k$  indices – employs the quadrature twice. For the purposes of the nonadiabatic relativistic correction, a 40-point quadrature was used.

Eventually, for a given basis size  $N$ , eight different sets had to be optimised. This is because one obviously uses a finite, not complete basis set, which, optimised for one quantity (e.g.  $\mathcal{E}(R)$ ), is not necessarily optimal for describing the others. It is particularly evident in the case of Gaussian basis functions, with their incorrect analytical properties. Thus, it is much better to prepare several separate sets for different applications. The first two sets – with cusp (5.34) and without it (5.33) – correspond to optimisation of the ground state energy  $\mathcal{E}(R) = \langle \psi | H | \psi \rangle$ . The next four basis sets are optimised to describe the intermediate states<sup>7</sup> in the following matrix elements

$$\langle \psi | [H^{(4,0)}]_r \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} [H^{(4,0)}]_r | \psi \rangle, \quad (5.45)$$

$$\langle \psi | \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) | \psi \rangle, \quad (5.46)$$

$$\langle \psi | \vec{n} \times \vec{\nabla}_R (V) \frac{1_{\Pi}}{(\mathcal{E} - H)} \vec{n} \times \vec{\nabla}_R (V) | \psi \rangle, \quad (5.47)$$

$$\langle \psi | [\vec{\nabla}_R^2 (V)]_r \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} [\vec{\nabla}_R^2 (V)]_r | \psi \rangle. \quad (5.48)$$

The last two basis sets are optimised for

$$\langle \psi_a | \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \cdot \vec{\nabla}_R (V - \mathcal{E}) | \psi_a \rangle, \quad (5.49)$$

$$\langle \vec{\psi}_a | \vec{n} \times \vec{\nabla}_R (V) \frac{1_{\Sigma^+}}{(\mathcal{E} - H)'} \vec{n} \times \vec{\nabla}_R (V) | \vec{\psi}_a \rangle. \quad (5.50)$$

These eight sets are needed to properly describe, respectively:  $|\psi\rangle$ ,  $|\psi\rangle$  (if standing next to  $[H^{(4,0)}]_r$ ),  $|\psi_{\text{rel}}\rangle$ ,  $|\psi_a\rangle$ ,  $|\vec{\psi}_a\rangle$ ,  $|\psi_{\text{na},1}\rangle$ ,  $|\psi_{\text{na},2}\rangle$ , and  $|\psi_{\text{na},3}\rangle$  functions, which appear in the elementary expressions presented in the last section of Chapter 4. The symmetric form of the quantities (5.45–5.50) ensures that they can be optimised variationally.

Note that Eq (5.48) involves master integrals requiring a single numerical integration, whereas Eq (5.45) relies on using the quadrature even twice. The necessity to do this

<sup>7</sup>See Eq. (4.10).

during each optimisation step is obviously a bottleneck of the calculations. Nonetheless, it is still nowhere near the cost of the ECE algorithm presented in the previous section.

To ensure proper subtraction of the ground state from the reduced resolvents, each  $\Sigma^+$  basis<sup>8</sup> was augmented with a fixed sector consisting of  $N/2$  basis functions optimised for the ground state without a cusp. Its nonlinear variational parameters were kept constant and were not optimised further.

The resolvents appearing both in the elementary expressions  $V_i$ ,  $X_i$ ,  $Y_i$ ,  $Z_i$ , and in the expressions presented above, can be taken into account by acting on the respective formulas with  $(\mathcal{E} - H)$  and solving the ensuing equation. A general form of such expression is

$$\langle \psi | \hat{O}_i \frac{1}{(\mathcal{E} - H)'} \hat{O}_i | \psi' \rangle = \langle \psi | \hat{O}_i | \psi_{\text{opt}} \rangle, \quad (5.51)$$

$$| \psi_{\text{opt}} \rangle = \frac{1}{(\mathcal{E} - H)'} \hat{O}_i | \psi' \rangle. \quad (5.52)$$

Then

$$(\mathcal{E} - H) | \psi_{\text{opt}} \rangle = \hat{O}_i | \psi' \rangle - | \psi \rangle \langle \psi | \hat{O}_i | \psi' \rangle. \quad (5.53)$$

With wave functions expanded in basis sets, it takes the form of a matrix equation:

$$(\mathbf{H} - \mathcal{E}\mathbf{S})\tilde{\mathbf{c}}_{\text{opt}} = -\mathbf{O}\mathbf{c}_{\psi'} + \mathbf{S}\tilde{\mathbf{c}}_{\psi}(\tilde{\mathbf{c}}_{\psi}^{\mathbf{T}}\mathbf{O}\mathbf{c}_{\psi'}), \quad (5.54)$$

where  $\mathbf{c}_{\psi}$  is a vector with the expansion coefficients of  $|\psi\rangle$ ,  $\mathbf{c}_{\text{opt}}$  – of  $|\psi_{\text{opt}}\rangle$ ,  $\mathbf{c}_{\psi'}$  – of  $|\psi'\rangle$ , and the tilde was introduced to distinguish between different basis sets<sup>9</sup>. We solve the equation for  $\tilde{\mathbf{c}}_{\text{opt}}$  using a Cholesky solver [71]. Note that the  $(\mathbf{H} - \mathcal{E}\mathbf{S})$  matrix is singular, which potentially requires choosing a different solving method because the Cholesky decomposition assumes the positive-definiteness of the matrix. This problem is often resolved by adding a small shift to  $\mathcal{E}$  to avoid the singularity. If the shift is small enough, it does not change the result significantly – but it certainly adds some ambiguity to the calculations. Alternatively, a dyadic matrix of the form  $\mathbf{D} \equiv (\mathbf{S}\tilde{\mathbf{c}}_{\psi})(\mathbf{S}\tilde{\mathbf{c}}_{\psi})^{\mathbf{T}}$  – which is just a  $|\psi\rangle\langle\psi|$  expanded in a basis – can be introduced, leading to the following equation

$$(\mathbf{H} - \mathcal{E}(\mathbf{S} \pm \mathbf{D}))\tilde{\mathbf{c}}_{\text{opt}} = -\mathbf{O}\mathbf{c}_{\psi'} + \mathbf{S}\tilde{\mathbf{c}}_{\psi}(\tilde{\mathbf{c}}_{\psi}^{\mathbf{T}}\mathbf{O}\mathbf{c}_{\psi'}). \quad (5.55)$$

The sign before  $\mathbf{D}$  depends on the sign of the energy (they are opposite)– to ensure the positive-definiteness of the  $(\mathbf{H} - \mathcal{E}(\mathbf{S} \pm \mathbf{D}))$  matrix. The addition of  $\mathbf{D}$  does not change the solution because  $|\psi_{\text{opt}}\rangle$  is orthogonal to the ground state by definition (5.52). At the same time, the problematic matrix singularity is removed. In general,  $\mathbf{D}$  could be multiplied by an arbitrary constant without changing the result. On the other hand, with finite numerical precision there is a possibility that for values of such a prefactor that are large or small enough, the result *would change*. Thus, the ‘physical’ choice of  $\mathbf{D}$  being multiplied by  $\pm\mathcal{E}$  seems the safest compromise.

<sup>8</sup>The  $\Pi$  bases are obviously orthogonal to the ground state by default.

<sup>9</sup>The one with the tilde is the  $N/2$ -augmented one for the description of the resolvent.

## 5.4 Results

The calculations were performed for three different basis sizes:  $N = 128, 256, 512$ , to observe numerical convergence and estimate the corresponding uncertainty. The electronic  $\mathcal{E}^{(4,1)}(R)$  potential was calculated for 59 points in the  $R$  range of 0–8 a.u. At first, additional points for greater internuclear distances had also been considered, but beyond 8 a.u. it was increasingly hard to achieve convergence. The results for the largest basis are presented in Table 5.2 and plotted in Fig. 5.2. They have already been reported in our paper [47]. The number of significant digits shown in Table 5.2 is tentative, the systematic uncertainty assessment was performed for the final results (see Chapter 6).

A curious quality of the potential – standing out in Fig. 5.2 – is the ‘cusp’ that appears for small internuclear distances. It seems that it is produced by partial cancellation when various components of  $\mathcal{E}^{(4,1)}(R)$  are added together. Actually, in the preliminary results, where the calculation grid was more sparse in that region, it was not visible. Extrapolation of the potential to  $R \rightarrow 0$  was erratic – with the value highly dependent on the extrapolation scheme. However, after refining the grid by adding additional small- $R$  points, the extrapolation stabilised on a value close to the one that can be deduced from the helium relativistic recoil calculations. Thus the value at  $R = 0$ ,  $2\mu_n \mathcal{E}^{(4,1)}(0) = -1.07969$  a.u. [34], has been added to the potential presented in Table 5.2. For  $R \rightarrow \infty$ , the potential behaves like  $\sim 1/R^4$ , as mentioned earlier. The value of the corresponding coefficient could not be reconciled with Ref. [57] however, possibly due to insufficient quality of the long-range points.

Table 5.2: The mass-independent nonadiabatic relativistic correction  $2\mu_n\mathcal{E}^{(4,1)}$  (in a.u.) for different values of the internuclear distance  $R$  (in a.u., for 512 basis size). A tentative number of significant digits shown.

R	$2\mu_n\mathcal{E}^{(4,1)}$	R	$2\mu_n\mathcal{E}^{(4,1)}$	R	$2\mu_n\mathcal{E}^{(4,1)}$	R	$2\mu_n\mathcal{E}^{(4,1)}$
0.0	-1.079 69	1.2	-0.486 52	2.1	-0.122 89	4.0	0.063 08
0.05	-0.761	1.3	-0.437 70	2.15	-0.107 12	4.2	0.048 65
0.1	-0.512	1.4	-0.390 85	2.2	-0.091 78	4.4	0.036 55
0.15	-0.385	1.45	-0.368 28	2.3	-0.062 21	4.6	0.027 37
0.2	-0.383 9	1.5	-0.346 24	2.4	-0.034 67	4.8	0.020 32
0.25	-0.433 6	1.6	-0.304 09	2.5	-0.008 80	5.0	0.015 45
0.3	-0.505 79	1.65	-0.283 70	2.6	0.014 69	5.2	0.011 82
0.4	-0.630 36	1.7	-0.263 96	2.7	0.035 88	5.4	0.009 19
0.5	-0.702 97	1.75	-0.244 62	2.8	0.054 42	5.6	0.007 30
0.6	-0.725 41	1.8	-0.225 83	2.9	0.069 94	5.8	0.005 90
0.7	-0.713 63	1.85	-0.207 76	3.0	0.082 16	6.0	0.004 91
0.8	-0.681 06	1.9	-0.189 95	3.2	0.097 14	6.5	0.003 13
0.9	-0.637 11	1.95	-0.172 52	3.4	0.099 47	7.0	0.002 05
1.0	-0.587 82	2.0	-0.155 56	3.6	0.091 98	7.5	0.001 43
1.1	-0.537 03	2.05	-0.139 04	3.8	0.078 60	8.0	0.001 11

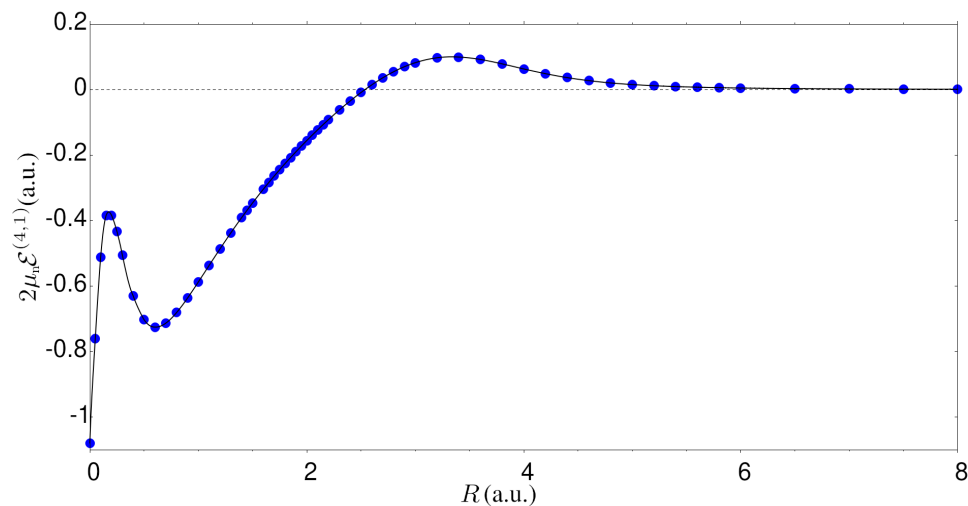


Figure 5.2: Mass-independent nonadiabatic relativistic correction  $2\mu_n\mathcal{E}^{(4,1)}$  for the ground electronic state as a function of the internuclear distance  $R$ .



# Solving the nuclear equation

For all the NRQED/NAPT contributions presented in Chapter 3, the electronic part of the problem is much more complex than the nuclear one, both in terms of derivation of formulas and computations. Nevertheless, all it produces are  $R$ -dependent corrections to the potential in which the nuclei move. To be able to compare with the experiment, the nuclear problem still has to be solved. The radial nuclear Schrödinger equation in the BO approximation has already been shown (3.12, 3.44)

$$H_N \chi(R) = E^{(2,0)} \chi(R), \quad (6.1)$$

$$H_N = -\frac{1}{2\mu_n} \frac{d^2}{dR^2} + \mathcal{E}(R) + \frac{J(J+1)}{2\mu_n R^2}. \quad (6.2)$$

As a second-order ordinary differential equation, there are many possible methods to solve it numerically. For our needs, we can solve it with a Discrete Variable Representation method [72] and obtain a numerical representation of  $\chi(R)$  (as well as the corresponding energy). Together with all the  $R$ -dependent corrections to the  $\mathcal{E}(R)$  potential available – obtained as described in Chapter 3 – it is then used to calculate the contributions to the rovibrational energy.

## 6.1 Discrete Variable Representation

The Discrete Variable Representation (DVR) method is a relatively simple algorithm, being efficient and accurate at the same time. It is a pseudo-spectral method, making use of both the discrete grid and a basis set. There are many different flavours of DVR – using various basis sets and crafted for different integration ranges. For the needs of the thesis (as well as in Ref. [47]), the Fourier-basis version proposed by Colbert and Miller in Ref. [72] is employed. It assumes the following expansion of the radial nuclear wave

function in a basis

$$\chi(R) = \sum_{n=1}^N f_n \phi_n(R), \quad (6.3)$$

where  $\phi_n(R)$  are Fourier particle-in-a-box functions

$$\phi_n(R) = \left( \frac{2}{b-a} \right)^{1/2} \sin \left[ \frac{n\pi(R-a)}{b-a} \right], \quad (6.4)$$

and where  $R \in [a, b]$ . The coefficients  $f_n$  can be expressed via a numerical quadrature with weights  $w_n$

$$f_n = \sum_{m=1}^N w_n \phi_n(R_m) \chi(R_m), \quad (6.5)$$

It is worth noticing that the position  $R$  is discretised on  $N$  points – equal to the number of basis functions  $\phi_n$

$$R_m = a + \frac{m(b-a)}{N+1}, \quad \Delta R = \frac{b-a}{N+1}, \quad (6.6)$$

for  $m = 1, \dots, N$  (which means that  $a$  is not a grid point itself). The weights  $w_n$  are all equal to the grid separation  $\Delta R$  in this type of DVR [73]. Combining Eqs (6.3, 6.5) together, one gets

$$\begin{aligned} \chi(R) &= \sum_{n=1}^N \sum_{m=1}^N \Delta R \phi_n(R_m) \chi(R_m) \phi_n(R) \\ &= \sum_{m=1}^N \chi_m \varphi_m(R), \end{aligned} \quad (6.7)$$

where  $\varphi_m(R)$  is a DVR orthonormal position basis<sup>1</sup> and  $\chi_m$  is proportional to the value of the wave function on the  $R_m$  grid point

$$\varphi_m(R) = \sum_{n=1}^N \phi_n(R_m) \phi_n(R) \sqrt{\Delta R}, \quad (6.8)$$

$$\chi_m = \chi(R_m) \sqrt{\Delta R}. \quad (6.9)$$

Note that for the radial basis functions defined by Eq. (6.4)

$$\sum_{n=1}^N \phi_n(R_m) \phi_n(R) = \frac{2}{b-a} \sum_{n=1}^N \sin \left[ \frac{n\pi(R_m-a)}{b-a} \right] \sin \left[ \frac{n\pi(R-a)}{b-a} \right], \quad (6.10)$$

<sup>1</sup>Not to be confused with the basis (6.4) in which the radial function  $\chi$  is expanded.

which for  $(b - a) \rightarrow \infty$  and  $N \rightarrow \infty$  tends to a sinc function [72]

$$\lim_{\substack{b-a \rightarrow \infty \\ N \rightarrow \infty}} \sum_{n=1}^N \phi_n(R_m) \phi_n(R) = \frac{\sin[\pi(R - R_m)/\Delta R]}{\pi(R - R_m)} = \frac{1}{\Delta R} \text{sinc}[\pi(R - R_m)/\Delta R]. \quad (6.11)$$

This is why this type of DVR is also known as the *sinc DVR* [73]. What is more important here, the above limit tends to  $1/\Delta R$  on the  $m$ -th grid node ( $R = R_m$ ) and to 0 on other nodes, and if also  $\Delta R \rightarrow 0$  – it tends to Dirac  $\delta(R - R_m)$  [72]. The impact of these asymptotic properties should not be overlooked – as Eqs (6.8, 6.11) imply

$$\varphi_n(R_m) = \frac{\delta_{nm}}{\sqrt{\Delta R}}. \quad (6.12)$$

That is why the potential<sup>2</sup> energy matrices in the  $\varphi_n$  DVR basis are diagonal

$$V_{ij} = \sum_{n=1}^N \Delta R \varphi_i(R_n) V(R_n) \varphi_j(R_n) = \sum_{n=1}^N \delta_{in} \delta_{jn} V(R_n) = \delta_{ij} V(R_j), \quad (6.13)$$

and

$$\begin{aligned} \langle \chi | V | \chi \rangle &\approx \sum_{n=1}^N \sum_{i=1}^N \sum_{j=1}^N \Delta R \chi_i \chi_j V(R_n) \varphi_i(R_n) \varphi_j(R_n) \\ &= \sum_{n=1}^N \sum_{i=1}^N \sum_{j=1}^N \chi_i \chi_j V(R_n) \delta_{in} \delta_{jn} \\ &= \sum_{n=1}^N \chi_n \chi_n V(R_n). \end{aligned} \quad (6.14)$$

The interval of  $R$  in our problem is  $[0, \infty)$ , so  $a = 0$ ,  $b \rightarrow \infty$ ,  $N \rightarrow \infty$ , and  $R_m = m\Delta R$ . Obviously, in practical applications both  $b$  and  $N$  have to be finite, but even as small as  $N = 160$  and  $b = 8.0$  are usually sufficient for most of our purposes. They only need to be increased when investigating highly excited vibrationally states.

In fact, the property (6.12) does not depend<sup>3</sup> on the choice of the basis set  $\varphi_n$  – it is assumed when constructing a DVR, and it is required from the basis set to fulfill it. There are thus different possible types of DVR, with different basis sets, grids, and weights [73]. The explicit form of the basis set is needed mainly to derive matrices of operators involving differentiation, such as the kinetic energy or momentum operators. They cannot be treated as simply as in Eq. (6.14), and their matrices are not diagonal. Fortunately, they can still be expressed by very simple formulas, as shown in Refs [72, 74]

$$D_{ij} = -\frac{1}{\Delta R} (-1)^{i-j} \left\{ \begin{array}{ll} \frac{1}{2i}, & \text{for } i = j \\ \frac{1}{j-i} + \frac{1}{i+j}, & \text{for } i \neq j \end{array} \right\} \quad (6.15)$$

<sup>2</sup>Again, in the context of our problem, ‘potential’ can be understood as  $\mathcal{E}(R)$  or as a correction to it.

<sup>3</sup>Up to the multiplicative constant, which depends on the choice of the weights  $w_n$ .

for the differentiation operator  $\hat{D} = d/dR$ , and

$$T_{ij} = \frac{1}{2\mu_n \Delta R^2} (-1)^{i-j} \left\{ \begin{array}{ll} \frac{\pi^2}{3} - \frac{1}{2i^2}, & \text{for } i = j \\ \frac{2}{(i-j)^2} - \frac{2}{(i+j)^2}, & \text{for } i \neq j \end{array} \right\} \quad (6.16)$$

for the kinetic energy. Thus, the Hamiltonian in the BO approximation is

$$H_{ij} = \left\{ \begin{array}{ll} \frac{1}{2\mu_n \Delta R^2} \left( \frac{\pi^2}{3} - \frac{1}{2i^2} \right) + \frac{J(J+1)}{2\mu_n R_i^2} + \mathcal{E}(R_i), & \text{for } i = j \\ \frac{1}{2\mu_n \Delta R^2} (-1)^{i-j} \left( \frac{2}{(i-j)^2} - \frac{2}{(i+j)^2} \right), & \text{for } i \neq j \end{array} \right\}. \quad (6.17)$$

It is no surprise that the nonadiabatic Eq. (3.34) leads to a more elaborate formula – not only because of the ‘distance-dependent masses’  $\mathcal{W}_{\parallel}(R)$  and  $\mathcal{W}_{\perp}(R)$  present, but also because  $\mathcal{W}_{\parallel}(R)$  is subjected to differentiation

$$H_{ij} = \left\{ \begin{array}{ll} \frac{1}{\Delta R^2} \left( \frac{1}{2\mu_a} + \mathcal{W}_{\parallel}(R_i) \right) \left( \frac{\pi^2}{3} - \frac{1}{2i^2} \right) + \frac{\mathcal{W}'_{\parallel}(R_i)}{R_i} + \frac{\mathcal{W}''_{\parallel}(R_i)}{2} \\ \quad + \left( \frac{1}{2\mu_a} + \mathcal{W}_{\perp}(R_i) \right) \frac{J(J+1)}{R_i^2} + \mathcal{Y}(R_i), & \text{for } i = j \\ \frac{(-1)^{i-j}}{2\Delta R^2} \left( \frac{1}{\mu_a} + \mathcal{W}_{\parallel}(R_i) + \mathcal{W}_{\parallel}(R_j) \right) \left( \frac{2}{(i-j)^2} - \frac{2}{(i+j)^2} \right), & \text{for } i \neq j \end{array} \right\}. \quad (6.18)$$

where  $\mathcal{W}'_{\parallel}$  and  $\mathcal{W}''_{\parallel}$  are the first and second derivatives of  $\mathcal{W}_{\parallel}$  with respect to  $R$ . It is worth noting that if we choose to calculate energy levels with respect to the dissociation limit, from all the ‘potentials’ their value for  $R \rightarrow \infty$  (which corresponds to two non-interacting hydrogen atoms) has to be subtracted. This is also why in Eq. (6.18) the reduced nuclear mass  $\mu_n$  is replaced with the reduced mass  $\mu_a$  of two hydrogen atoms

$$\frac{1}{\mu_a} = \frac{1}{m_A + m} + \frac{1}{m_B + m}. \quad (6.19)$$

As discussed in Refs [39, 41],  $\mathcal{W}'_{\parallel}$  and  $\mathcal{W}'_{\perp}$  tend to  $-\frac{m}{4\mu_n}$  for  $R \rightarrow \infty$ , reproducing the leading terms of the  $\frac{1}{2\mu_a}$  expansion in the electron-nuclear mass ratio.

## 6.2 H2spectr

I hope that the previous chapters have given at least some credit to how dynamic the progress in the field of H<sub>2</sub> spectroscopy has been in recent years – with new corrections calculated each year. It becomes a challenge to organise and update all this data – and to distribute it amongst the interested spectroscopists efficiently. For these reasons, the idea of the `H2spectr` Fortran program has been conceived. After all, it is much more effective to update several files containing correction potentials than to recalculate all the possible energies that can be of interest, each time a new result appears. Solving the radial nuclear equation, the program complements the `H2SOLV` code, also developed in our group [43] – which solves the electronic Schrödinger equation in a KW basis.

From the mathematical point of view, `H2spectr` solves the Schrödinger nuclear equation with the Born-Oppenheimer Hamiltonian (6.17) to obtain its eigenvalues  $E^{(2,0)}$  and eigenfunctions  $\chi(R)$  in a DVR representation. These, in turn, are used to calculate all the needed expectation values of corrections to the electronic potential, as described in Chapter 3. They are transformed to a DVR form, using Eq.(6.14)

$$E^{(4,0)} = \sum_{i=1}^N \chi_i^2 \mathcal{E}^{(4,0)}(R_i), \quad (6.20)$$

$$E^{(4,1)} = \sum_{i=1}^N \chi_i^2 \mathcal{E}^{(4,1)}(R_i) + 2 \sum_j^N \frac{\left( \sum_{i=1}^N \chi_i \chi_i^{(j)} \mathcal{E}^{(4,0)}(R_i) \right) \left( \sum_{i=1}^N \chi_i \chi_i^{(j)} \mathcal{E}^{(2,1)}(R_i) \right)}{E^{(2,0)} - E_j^{(2,0)}}, \quad (6.21)$$

$$E^{(4)} = E^{(4,0)} + E^{(4,1)}, \quad (6.22)$$

$$E^{(5)} = \sum_{i=1}^N \chi_i^2 \mathcal{E}^{(5,0)}(R_i), \quad (6.23)$$

$$E^{(6)} = \sum_{i=1}^N \chi_i^2 \mathcal{E}^{(6,0)}(R_i) + \sum_j^N \frac{\left( \sum_{i=1}^N \chi_i \chi_i^{(j)} \mathcal{E}^{(4,0)}(R_i) \right)^2}{E^{(2,0)} - E_j^{(2,0)}}, \quad (6.24)$$

$$E^{(7)} = \sum_{i=1}^N \chi_i^2 \mathcal{E}^{(7,0)}(R_i), \quad (6.25)$$

$$E_{\text{FS}} = \sum_{i=1}^N \chi_i^2 \mathcal{E}_{\text{FS}}(R_i), \quad (6.26)$$

$$E_{\text{tot}} = E^{(2)} + E^{(4)} + E^{(5)} + E^{(6)} + E^{(7)} + E_{\text{FS}}, \quad (6.27)$$

where  $\chi_i^{(j)}$  denotes  $\chi_i$  (6.9) for the  $j$ -th excited vibrational state. The potentials are taken from the best sources available at the time, respectively:  $\mathcal{E}^{(4,0)}(R)$  – Ref. [23],  $\mathcal{E}^{(4,1)}(R)$  – Ref. [47], and  $\mathcal{E}^{(6,0)}(R)$  – Ref. [22].  $\mathcal{E}^{(7,0)}(R)$  and  $\mathcal{E}_{\text{FS}}(R)$  use the electron-nucleus Dirac  $\delta$  results obtained in Ref. [23]. The leading QED contribution  $\mathcal{E}^{(5,0)}(R)$  combines the results from several works – Bethe logarithm expectation values from Ref. [21], Dirac  $\delta$  (electron-electron and electron-nucleus) from Ref. [23], and the Araki-Sucher term calculated as a part of Ref. [22] (not explicitly published there).

After testing different interpolation schemes, piecewise B-spline interpolation [75] was chosen to obtain values of all the above potentials at DVR grid points, combined with simple long-range fits to reproduce their asymptotic behaviour. Sixth-order splines are used for all the potentials, except for  $\mathcal{E}^{(4,1)}(R)$ , where third-order splines prove to be optimal. The most problematic one to interpolate is the relativistic BO  $\mathcal{E}^{(4,0)}(R)$ . Its short-range behaviour requires splines of order as high as the twelfth to reproduce it properly, which – in turn – poses the danger of introducing artificial oscillations. Fortunately, multiplying

the potential by  $R^4$  before interpolation allows us to reduce the order to the mentioned sixth. The tradeoff – a potentially greater error introduced this way to the short-range points – is definitely an agreeable price to be paid, because these points contribute significantly less to the overall result (nuclear wave functions decay rapidly for short ranges). The interpolation is performed by the program itself – using the PPPACK library [75] – from the potentials taken directly<sup>4</sup> from the sources mentioned. In future, the interpolation error currently present may potentially be eliminated by finding analytic fits to the above potentials. In the case of  $\mathcal{E}(R) \equiv \mathcal{E}^{(2,0)}(R)$  and  $\mathcal{E}^{(2,1)}(R)$ , the fits are available already. The one for  $\mathcal{E}^{(2,1)}(R)$  was published in Ref. [44] (supplementary material). For  $\mathcal{E}(R)$ , a fit was constructed using the results from Ref. [18]; it has not been published before, but will be included in our upcoming paper [76].

Regarding  $E^{(2)}$ , its BO approximation ( $E^{(2,0)}$ ) is surely not accurate enough to be used in Eq. (6.27). That is why either a (highly accurate) result of the fully nonadiabatic calculations (e.g. [45], [17]) is provided or – if not available – the nuclear Schrödinger equation is solved again – but this time with the NAPT-corrected Hamiltonian (6.18). The additional terms needed in this step:  $\mathcal{W}_{\parallel}(R_i)$ ,  $\mathcal{W}'_{\parallel}(R_i)$ ,  $\mathcal{W}''_{\parallel}(R_i)$ ,  $\mathcal{W}_{\perp}(R_i)$ ,  $\delta\mathcal{E}_{\text{na}}(R)$ , are taken from Ref. [40] (in a form of analytic fits), whereas for the unique heteronuclear-molecule term  $\delta\mathcal{E}'_{\text{na}}(R)$ , a fit was constructed [76] based on the data from Ref. [41].

The core of the program is the subroutine `level(qv,qj,isot,nonrel,N,ran,output)` (for its source code, see the disk attached to the thesis). It returns `output`, a variable of the `output` derived type, which stores<sup>5</sup> all the energy components listed in Eqs (6.20–6.27), as well as their error estimates:

- `output%E2full` – the fully nonadiabatic nonrelativistic energy,
- `output%E2napt` – the nonrelativistic energy in the NAPT approach (6.18),
- `output%E2` – one of the above, depending how `nonrel` is set,
- `output%E2na` – an approximate value of  $E^{(2,2)}$ , used to estimate the NAPT error<sup>6</sup>,
- `output%E4` – the total relativistic energy `output%E4bo+output%E4na+output%E4sec`,
- `output%E4bo` – the relativistic BO correction (6.20),
- `output%E4na` – the first term in  $E^{(4,1)}$  in Eq. (6.21),
- `output%E4sec` – the second term in  $E^{(4,1)}$  in Eq. (6.21),
- `output%E5` – the  $E^{(5)}$  leading QED correction (6.23),
- `output%E6` – the total  $E^{(6)}$  HQED correction (6.24),
- `output%E6bo` – the first term in  $E^{(6)}$  (6.24),
- `output%E6sec` – the second term in  $E^{(6)}$  (6.24),
- `output%E7` – the  $E^{(7)}$  HQED correction (6.25),
- `output%Efs` – the finite-nucleus-size correction (6.26),

<sup>4</sup>With a small, interesting exception. In some cases, very closely lying points (for  $R \in \{1.4, 1.4011\}$  a.u.) were available. Removing one of them before the interpolation stabilised it (reduced the impact of changing the order of the interpolating polynomial).

<sup>5</sup>As double-precision real numbers.

<sup>6</sup>Calculated as  $E^{(2)} - E^{(2,0)} - E^{(2,1)}$ .

- `outp%Etot` – the total energy of the rovibrational level (6.27),
- `outp%errE2` – the nonrelativistic energy uncertainty,
- `outp%errE4` – the total relativistic energy ( $E^{(4)}$ ) uncertainty,
- `outp%errE5` – the leading QED ( $E^{(5)}$ ) correction uncertainty,
- `outp%errE6` – the  $E^{(6)}$  HQED correction uncertainty,
- `outp%errE7` – the  $E^{(7)}$  HQED correction uncertainty,
- `outp%errEfs` – the finite-nucleus-size correction uncertainty,
- `outp%errEtot` – the total energy uncertainty,
- `outp%rerr` – the uncertainty due to finite accuracy of the nuclear charge radii,
- `outp%E2which` – indicates the `outp%E2` calculation type ("FULL"/"NAPT"/"BO" /"NAN" ),
- `outp%pm` – the reduced nuclear mass  $\mu_n$  in use,
- `outp%wav` – an array with values of the wave function on the DVR grid points and the corresponding distances:  $\{R_i, \chi(R_i)\}$ .

The user provides the vibrational (`qv`) and rotational (`qj`) quantum numbers to identify the rovibrational state, as well as the isotopic composition of the molecule (`isot="H2"/"D2"/"T2"/"HD"/"HT"/"DT"/"PC"`)<sup>7</sup>, the number of DVR grid points (`N`), the DVR integration range (`ran`), and the information on how the nonrelativistic calculation should be handled (`nonrel`). That last parameter can be one of the following:

- "A" – both the fully nonadiabatic energy `E2full` is sought (in an external file `data/<isot>.dat`, in a 'qv qj E2full [a.u.]' format) and the NAPT one (`E2napt`) is calculated; if `E2full` could be found, `E2=E2full`, otherwise `E2=E2napt`,
- "N" – only the NAPT energy is calculated,
- "B" – only the BO energy is calculated (very inaccurate) and stored in `E2=E2napt`,
- "F" – only the fully nonadiabatic energy is sought.

The error estimation subroutine is provided below

```
subroutine errors(oin)
USE,INTRINSIC :: IEEE_ARITHMETIC
!Calculates error estimates of "oin".
!E2 estimate based on calculation method.
implicit none
type(output),intent(inout)::oin
select case(oin%E2which)
case("NAPT")
oin%errE2=abs(oin%Ena)/oin%pm
case("BO")
oin%errE2=IEEE_VALUE(oin%errE2,IEEE_QUIET_NAN)
case("FULL")
oin%errE2=1.d-7
case default
oin%errE2=IEEE_VALUE(oin%errE2,IEEE_QUIET_NAN)
end select
!Errors estimated as (contribution x 1/pm) - due to the neglected higher
!finite-nuclear-mass effects. E4, E5, and E6 contain additional numerical
!error. E7, known only roughly, hence 25% error estimate.
```

<sup>7</sup>"PC" prints the physical constants used by the program and quits.

```

oin%errE4=sqrt((oin%E4bo*1.9d-6)**2+((oin%E4na+oin%E4sec)/oin%pm)**2 &
    +(oin%E4na*2.d-4)**2)
oin%errE5=sqrt((oin%E5/oin%pm)**2+(oin%E5*5.1d-4)**2)
oin%errE6=sqrt((oin%E6bo*2.9d-3)**2+(oin%E6/oin%pm)**2)
oin%errE7=abs(oin%E7)*0.25d0
oin%errEfs=sqrt((oin%Efs/oin%pm)**2+(oin%Efs*oin%rerr)**2)
oin%errEtot=sqrt(oin%errE2**2+oin%errE4**2+oin%errE5**2+oin%errE6**2 &
    +oin%errE7**2+oin%errEfs**2)
end subroutine

```

It is based on the assumption that there should be a term of the next order in  $m/\mu_n$  missing for all the contributions. In the estimates for  $E^{(4)}$ ,  $E^{(5)}$ , and  $E^{(6)}$ , there are additional terms added to account for the numerical uncertainty of the respective potentials, whereas in  $E_{FS}$  – of the nuclear charge radii. `errE7` is set to 25% of the `E7` value because the expression for  $E^{(7)}$  is known only approximately, so a conservative estimate is needed.

Basic arithmetic operations are defined for the `output` type, allowing easy calculation of transition energies, as presented in the following simple example

```

PROGRAM H2SPECTR_PRESENTATION1
  use h2spectr_types
  implicit none
  type(output) :: lvl_1, lvl_2, trans
  !A simple example, where two rovibrational levels of HD are calculated.
  !Then their difference is taken -- to produce the (2,2)->(0,1) transition
  !energy. The total transition energy, as well as the total uncertainty are
  !printed.
  call level(0,1,"HD","N",200,10.d0,lvl_1)
  call level(2,2,"HD","N",200,10.d0,lvl_2)
  trans=lvl_2-lvl_1
  write(*,*)"Etot, err"
  write(*,*)trans%Etot,trans%errEtot
  write(*,*)"E2 type: ",trans%E2which

  !Then the nonrelativistic energy (its value and an error estimation) is
  !updated with user-provided values and printed.
  !If E2 is updated, additionally E2which is set to "FULL".
  call update(trans,"E2",7241.84616822d0,2.d-8)
  write(*,*)"Etot, err (updated)"
  write(*,*)trans%Etot,trans%errEtot
  write(*,*)"E2 type: ",trans%E2which
END

```

It returns

```

Etot, err
  7241.8493827247721          9.9263398973008167E-004
E2 type: NAPT
Etot, err (updated)
  7241.8492951960106          3.6378172232210132E-005
E2 type: FULL

```

In the above example, when `trans=lvl_2-lvl_1` is executed, the total energy of the (0,1) rovibrational level, as well as all its contributions, are subtracted from their counterparts of the (2,2) level to produce the (2,2)  $\rightarrow$  (0,1) transition<sup>8</sup> energy. The uncertainty

<sup>8</sup>With the levels written in  $(v,J)$  convention, with  $v$ –vibrational quantum number,  $J$ –rotational quantum number.



estimates for the  $(2, 2) \rightarrow (0, 1)$  transition are automatically calculated at this point too.

As seen above, sometimes the user can have their own theoretical results. To facilitate the update, the subroutine (nomen omen) `update` is provided. The user just has to choose the container they want updated, the contribution and the new value, as well as its error estimate. The total energy will be updated automatically. In the above example, both of the levels involved have the nonrelativistic contribution, `E2`, calculated with the same method (NAPT, `nonrel="N"`). The program also handles the situations where it is not the case. If for at least one of them `E2` is calculated just in the NAPT approximation (`E2napt`), `E2` of the transition is calculated from their `E2napt` values, regardless of whether the other has `E2full` available. When in doubt, the `E2which` component can always be printed to check which approach is in use.

The subroutine employs `DSPEVX` – a LAPACK [77] procedure to solve the eigenproblem of the BO DVR Hamiltonian matrix (6.17). All the eigenvectors and eigenvalues are obtained in this step – they are needed for Eqs (6.21, 6.24) – to perform the summations over states. Then, if the NAPT nonrelativistic energy is requested, the `DSPEVX` subroutine is called again – this time with the NAPT DVR Hamiltonian matrix (6.18) and solving only for the energy of the  $qv$ -th,  $qj$ -th rovibrational state. Having all these components, the code performs Eqs. (6.20–6.27). Despite solving the equation possibly twice, with the default settings<sup>9</sup> the program can generate the data for Tables 6.3–6.8, presented in the next section (without complete basis set extrapolation, however), in a matter of about 4 seconds (see Appendix B).

To simplify use of `H2spectr`, the frontend `H2spectre.exe` is provided. It functions as a ‘black box’, requiring the user only to point the isotopomer and the transition energies (or energy levels) that they want to calculate. An example of an input file is given below.

```
H2  Transitions
0 1   0 0
3 5   0 3
1 0   0 0
```

It returns the energies for the  $(0, 1) \rightarrow (0, 0)$ ,  $(3, 5) \rightarrow (0, 3)$ , and  $(1, 0) \rightarrow (0, 0)$  transitions in  $H_2$ :

```
H2      Transitions

v' = 0   J' = 1   -->   v'' = 0   J'' = 0
  Total          118.4868142   7.3E-06
-----

v' = 3   J' = 5   -->   v'' = 0   J'' = 3
  Total          12559.749514   2.5E-03
-----

v' = 1   J' = 0   -->   v'' = 0   J'' = 0
  Total          4161.166222   9.1E-04
-----
```

<sup>9</sup>`N=200`, `ran=10.0`, double-precision arithmetics for the algebra and quadruple-precision for analytic fits evaluation.

Similarly, to calculate (0,0) and (0,1) energy levels and show all their components, the user has to input:

```
H2 Levels
0 0
0 1
```

and issue `H2spectre.exe -V 2 <input.txt` (where `input.txt` contains the above), which produces:

```
(Int. points= 200 , Int. range= 10.0)
```

```
-----
H2      Levels

v' = 0   J' = 0

Contribution   Value [cm-1]   Error [cm-1]
E2(NAPT)       36118.797675    4.8E-04
E4              -0.531212       2.4E-06
  E4(B0)        -0.533130
  E4(rec)        0.002369
  E4(2nd)        -0.000451
E5              -0.195021       2.3E-04
E6              -0.002058       6.4E-06
  E6(B0)        -0.002067
  E6(2nd)        0.000009
E7              0.000101        2.5E-05
Efs             -0.000031       4.4E-08
Total          36118.069454    5.3E-04
-----
```

```
v' = 0   J' = 1

Contribution   Value [cm-1]   Error [cm-1]
E2(NAPT)       36000.312413    4.9E-04
E4              -0.533796       2.4E-06
  E4(B0)        -0.535710
  E4(rec)        0.002362
  E4(2nd)        -0.000448
E5              -0.193998       2.3E-04
E6              -0.002049       6.4E-06
  E6(B0)        -0.002058
  E6(2nd)        0.000009
E7              0.000101        2.5E-05
Efs             -0.000031       4.4E-08
Total          35999.582640    5.4E-04
-----
```

The `-V` command-line argument used above controls the verbosity of the output (0-2, with default 0). Similarly, `-N` and `-R` flags can be used to change the default values (`N=200`, `ran=10.0` a.u.) of the number of DVR grid points and the integration range. The values of constants used in the program and, in particular, in the derivation of the nonadiabatic relativistic results presented in the next section, are presented in Table 6.1 They can be printed by issuing `H2spectre.exe` with the command-line option `-pc` or – more directly – by passing "PC" as the isotopomer to the `level` subroutine. All the results provided in the tables in the next section have been obtained with the `H2spectr` program.

Table 6.1: Fundamental constants used in the program and in derivation of the results presented in Tables 6.3–6.8.

Constant	Value	Description
$m_p/m$	1836.152 673 89(17)	proton-electron mass ratio [78]
$m_d/m$	3670.482 967 85(13)	deuteron-electron mass ratio [78]
$m_t/m$	5496.921 535 88(26)	triton-electron mass ratio [78]
$r_p$	0.84087(39) fm	proton rms charge radius [79]
$r_d$	2.12771(22) fm	deuteron rms charge radius [80]
$r_t$	1.759 1(363) fm	triton rms charge radius [81]
$\alpha$	$7.297 352 566 4(17) \times 10^{-3}$	fine-structure constant [78]
$R_\infty$	$10 973 731.568 508(65) \text{ m}^{-1}$	Rydberg constant [78]
$a_0$	52.917 721 067(12) pm	Bohr radius [78]

`H2spectr` is planned to be published soon [76]. In the current state, as attached to the thesis, it can be considered fully functional. However, there is still some room for development – analytic fits can be constructed for the rest of the potentials, as well as more of the fully adiabatic results can be added to the database in the `data/<isot>.dat` files in future.

### 6.3 Results

Following Ref. [47], additional refinement of the results has been performed. Having the correction potential  $\mathcal{E}^{(4,1)}(R)$  calculated for three different basis set sizes (128, 256, 512), extrapolation to the complete basis set limit was done. Using the relativistic BO correction potentials  $\mathcal{E}^{(4,0)}(R)$  for basis set sizes of 128, 256, 512 and 1024 – obtained from the authors of Ref. [23] – all the components of the total relativistic contribution (3.53, 3.65, recast below), could be treated in such a way

$$E^{(4)} = E^{(4,0)} + \langle \chi | \mathcal{E}^{(4,1)}(R) | \chi \rangle + 2 \langle \chi | \delta\chi \rangle, \quad (6.28)$$

$$|\delta\chi\rangle = \mathcal{E}^{(4,0)}(R) \frac{1}{(E^{(2,0)} - H_N)'} \mathcal{E}^{(2,1)}(R) |\chi\rangle. \quad (6.29)$$

The above terms:  $E^{(4,0)}$ ,  $2 \langle \chi | \delta\chi \rangle$ , and  $\langle \chi | \mathcal{E}^{(4,1)}(R) | \chi \rangle$ , were extrapolated separately, utilising the following model

$$E(N) = \frac{A}{N^k} + E(\infty), \quad (6.30)$$

where  $N$  is the basis set size and  $A$  and  $E(\infty)$  are fitted parameters. Observation of convergence of the individual terms motivated the choice of  $k = 2$  for  $\langle \chi | \mathcal{E}^{(4,1)}(R) | \chi \rangle$  and  $k = 3$  for the two other cases.

The total relativistic contribution  $E^{(4)}$  to the dissociation energy of  $\text{H}_2$ ,  $\text{HD}$ , and  $\text{D}_2$ , in comparison to fully nonadiabatic naECG results from Ref. [36], is shown in Table 6.2. The uncertainty of the values is calculated as shown in the listing of the error estimation subroutine of `H2spectr` in the previous section. In particular, the total uncertainty of  $E^{(4)}$  contains additionally the estimate of the neglected higher-order nonadiabatic corrections – approximated by  $E^{(4,1)}/\mu_n$ . The only notable exception is the uncertainty of  $\langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle$ , which is taken here as the difference between the extrapolated value and the result obtained in the largest basis set (512)<sup>10</sup>. The error bar of  $2\langle\chi|\delta\chi\rangle$  is not big enough to contribute here. The agreement between the NAPT and the fully nonadiabatic

Table 6.2: Convergence of  $\langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle$  contribution to the dissociation energy (in  $\text{cm}^{-1}$ ). The remaining components of  $E^{(4)}$ , Eq. (6.28), are also shown for completeness. The total uncertainty of  $E^{(4)}$  contains the estimate of the higher-order nonadiabatic corrections,  $E^{(4,1)}/\mu_n$ .

Basis	$\text{H}_2$	$\text{HD}$	$\text{D}_2$
128	0.002 375 81	0.001 793 79	0.001 205 45
256	0.002 370 18	0.001 789 61	0.001 202 70
512	0.002 368 64	0.001 788 46	0.001 201 94
$\infty$	0.002 368 1(5)	0.001 788 1(4)	0.001 201 7(2)
$2\langle\chi \delta\chi\rangle$	-0.000 451 1	-0.000 342 0	-0.000 230 9
$E^{(4,1)}$	0.001 917 1(5)	0.001 446 1(4)	0.000 970 8(2)
$E^{(4,0)}$	-0.533 129 4(11)	-0.531 333 7(11)	-0.529 178 4(11)
$E^{(4)}$	-0.531 212 3(24)	-0.529 887 6(16)	-0.528 207 6(12)
naECG [36]	-0.531 215 6(5)	-0.529 887 5(2)	-0.528 206 1(1)
Difference	+0.000 003 3(24)	+0.000 000 1(16)	-0.000 001 5(12)

results [36] is good, with their difference being far too small to contribute to the total theoretical error – as Tables 6.4–6.8 prove. It justifies the use of the NAPT approach, in particular the neglect of the heteronuclear term in Eq. (3.9) for  $\text{HD}$ , which – at first glance – could seem a bit dubious. Moreover, the complete basis set extrapolation error in  $E^{(4,1)}$  turns out to be significantly smaller than the uncertainty contributed by neglect of the higher-order effects, as well as smaller than the numerical error of  $E^{(4,0)}$ . For that reason, in the `H2spectr` program only the potential obtained in the biggest basis set (512) is used and only the estimated extrapolation error is included (confer the listing in the previous section and the footnote comment on this page). For the purposes of this thesis, however, all the results for  $E^{(4)}$  in Tables 6.4–6.8 are extrapolated in the same way as those in Table 6.2.

<sup>10</sup>In `H2spectr`, it is estimated as  $0.0002 \times \langle\chi|\mathcal{E}^{(4,1)}(R)|\chi\rangle$  – with the prefactor based on *these* results from Table 6.2.

The dissociation energy  $D_0$  of  $\text{H}_2$ , HD, and  $\text{D}_2$ , with all the NRQED components given explicitly, is presented in Table 6.3, whereas Tables 6.4–6.8 contain chosen rovibrational transitions for  $\text{H}_2$ , HD,  $\text{D}_2$ , DT, and  $\text{T}_2$ , compared to experimental data. All the energy levels are written in  $(v, J)$  convention, with  $v$ –vibrational quantum number,  $J$ –rotational quantum number. Note that the references provided in the last column point to the source of the potentials used to calculate it with `H2spectr`. The source of the values themselves is referred to only for experimental and fully nonadiabatic results. Note also that – compared to Ref. [47] – the interpolation procedure has been since improved, so both the error estimations and the last digits can differ for some of the values. Furthermore, recent calculations [82] suggest that the  $E^{(2)}$  values for the  $(3, 5) \rightarrow (0, 3)$  and  $(1, 0) \rightarrow (0, 0)$  transitions for  $\text{H}_2$  (Table 6.4) given in Ref. [23] (and cited in Ref. [47], as well as in the first version of this thesis) had significantly underestimated uncertainties. For that reason, they are replaced here with, respectively, a NAPT result obtained with `H2spectr` and a new fully nonadiabatic value [82].

In general, the theory-experiment agreement is good. However, there are cases such as the  $D_0$  value for HD (Table 6.3), all the  $R(J)$  transitions for HD in the lower part of the Table 6.5, and several  $Q(J)$  transitions for  $\text{T}_2$  (Table 6.8), where the discrepancy remains, and can be large ( $\approx 3\sigma$ ). They require further investigation.

Table 6.3: Contributions to the dissociation energy  $D_0$  of  $\text{H}_2$ , HD and  $\text{D}_2$  (in  $\text{cm}^{-1}$ ), in comparison to experimental values.

Con./ $(v, J)$	$\text{H}_2$	HD	$\text{D}_2$	References
$E^{(2)}$	36 118.797 746 10(3)	36 406.510 891 37(1)	36 749.090 990 99(2)	[17], [45], [36]
$E^{(4)}$	−0.531 212 3(24)	−0.529 888 6(16)	−0.528 207 6(12)	[44]+[23]+[47]
$E^{(5)}$	−0.194 910 4(2)	−0.196 53(19)	−0.198 31(15)	[24], [23]+[21]+[22]
$E^{(6)}$	−0.002 058(6)	−0.002 071(6)	−0.002 087(6)	[22]+[23]
$E^{(7)}$	0.000 101(25)	0.000 102(25)	0.000 103(26)	[23]
$E_{\text{FS}}$	−0.000 031	−0.000 116	−0.000 202	[23]
Total	36 118.069 636(26)	36 405.782 39(19)	36 748.362 28(15)	
Exp. 1.	36 118.069 62(37)	36 405.783 66(36)	36 748.362 86(68)	[15], [83], [26]
Diff. 1.	+0.000 02(37)	−0.001 27(41)	−0.000 58(70)	
Exp. 2.	36 118.069 45(31)			[16]
Diff. 2.	+0.000 19(31)			

Table 6.4: Contributions to the dissociation energy of the first rotationally excited level and to two selected transitions in H<sub>2</sub> (in cm<sup>-1</sup>), in comparison to experimental values.

Con./( $v, J$ )	(0, 1)	(3, 5) → (0, 3)	(1, 0) → (0, 0)	References
$E^{(2)}$	36 000.312 485 66(6)	12 559.750 0(25)	4 161.164 070 2(1)	[17], [40], [82]
$E^{(4)}$	-0.533 795 9(24)	0.065 878(1)	0.023 554	[44]+[23]+[47]
$E^{(5)}$	-0.193 887 7(11)	-0.065 811(79)	-0.021 317(26)	[24], [23]+[21]+[22]
$E^{(6)}$	-0.002 049(6)	-0.000 595(2)	-0.000 191(1)	[22]+[23]
$E^{(7)}$	0.000 101(25)	0.000 032(8)	0.000 010(3)	[23]
$E_{\text{FS}}$	-0.000 031	-0.000 010	-0.000 003	[23]
Total	35 999.582 823(26)	12 559.749 5(25)	4 161.166 123(26)	
Exp.	35 999.582 834(11)	12 559.749 52(5)	4 161.166 36(15)	[84], [85], [86]
Diff.	-0.000 011(28)	-0.000 0(25)	-0.000 14(15)	
Con./( $v, J$ )	(0, 1) → (0, 0)	(1, 1) → (0, 1)	(1, 2) → (0, 2)	References
$E^{(2)}$	118.485 260 44(4)	4 155.251 97(91)	4 143.463 81(91)	[17], [40], [40]
$E^{(4)}$	0.002 583 56(1)	0.023 333	0.022 894	[44]+[23]+[47]
$E^{(5)}$	-0.001 022 7(12)	-0.021 256(26)	-0.021 135(25)	[23]+[21]+[22]
$E^{(6)}$	-0.000 008 9	-0.000 191(1)	-0.000 190(1)	[22]+[23]
$E^{(7)}$	0.000 000 5(1)	0.000 010(3)	0.000 010(3)	[23]
$E_{\text{FS}}$	-0.000 000 2	-0.000 003	-0.000 003	[23]
Total	118.486 812 7(12)	4 155.253 86(91)	4 143.465 39(91)	
Exp.	118.486 8(1)	4 155.254 00(21)	4 143.465 53(15)	[87], [86], [86]
Diff.	+0.000 0(1)	-0.000 14(93)	-0.000 14(92)	
Con./( $v, J$ )	(11, 1) → (0, 0)	(11, 3) → (0, 0)	(11, 4) → (0, 0)	References
$E^{(2)}$	32 938.037 7(48)	33 186.775 2(47)	33 380.402 5(47)	[40]
$E^{(4)}$	-0.119 362(2)	-0.123 829(2)	-0.127 776(2)	[44]+[23]+[47]
$E^{(5)}$	-0.166 97(20)	-0.169 12(20)	-0.170 77(21)	[23]+[21]+[22]
$E^{(6)}$	-0.001 624(5)	-0.001 647(5)	-0.001 665(5)	[22]+[23]
$E^{(7)}$	0.000 083(21)	0.000 084(21)	0.000 085(21)	[23]
$E_{\text{FS}}$	-0.000 026	-0.000 026	-0.000 026	[23]
Total	32 937.749 8(48)	33 186.480 7(47)	33 380.102 4(47)	
Exp.	32 937.755 4(16)	33 186.479 1(16)	33 380.102 5(33)	[88]
Diff.	-0.005 6(51)	+0.001 6(50)	-0.000 1(57)	

Table 6.5: Contributions to selected transitions in HD (in  $\text{cm}^{-1}$ ), in comparison to experimental values.

Con./( $v, J$ )	(1, 0) $\rightarrow$ (0, 0)	(0, 1) $\rightarrow$ (0, 0)	(1, 1) $\rightarrow$ (0, 1)	References
$E^{(2)}$	3 632.158 204 27(1)	89.226 757 95(1)	3 628.302 279 75(1)	[45]
$E^{(4)}$	0.020 999	0.001 950 56	0.020 856	[44]+[23]+[47]
$E^{(5)}$	-0.018 641(18)	-0.000 770 93(74)	-0.018 601(18)	[23]+[21]+[22]
$E^{(6)}$	-0.000 167(1)	-0.000 006 68(2)	-0.000 167(1)	[22]+[23]
$E^{(7)}$	0.000 009(2)	0.000 000 37(9)	0.000 009(2)	[23]
$E_{\text{FS}}$	-0.000 010	-0.000 000 42	-0.000 010	[23]
Total	3 632.160 394(18)	89.227 930 85(75)	3 628.304 367(18)	
Exp.	3 632.160 52(22)	89.227 931 6(8)	3 628.304 50(22)	[86], [89], [86]
Diff.	-0.000 13(22)	-0.000 000 7(11)	-0.000 13(22)	
Con./( $v, J$ )	(2, 2) $\rightarrow$ (0, 1)	(2, 3) $\rightarrow$ (0, 2)	(2, 4) $\rightarrow$ (0, 3)	References
$E^{(2)}$	7 241.846 168 22(2)	7 306.479 554 52(2)	7 361.899 285 85(1)	[45]
$E^{(4)}$	0.040 927	0.041 927	0.042 559	[44]+[23]+[47]
$E^{(5)}$	-0.037 461(36)	-0.037 972(37)	-0.038 381(37)	[23]+[21]+[22]
$E^{(6)}$	-0.000 337(1)	-0.000 341(1)	-0.000 345(1)	[22]+[23]
$E^{(7)}$	0.000 018(5)	0.000 018(5)	0.000 019(5)	[23]
$E_{\text{FS}}$	-0.000 021	-0.000 021	-0.000 021	[23]
Total	7 241.849 295(36)	7 306.483 166(37)	7 361.903 117(37)	
Exp 1.	7 241.849 356 16(67)	7 306.483 227 84(93)	7 361.903 178 73(93)	[90]
Diff 1.	-0.000 061(36)	-0.000 061(37)	-0.000 061(37)	
Exp 2.	7 241.849 386(3)			[91]
Diff 2.	-0.000 092(36)			
Exp 3.	7 241.849 345 6(32)			[92]
Diff 3.	-0.000 051(36)			

Table 6.6: Contributions to selected transitions in D<sub>2</sub> (in  $\text{cm}^{-1}$ ), in comparison to experimental values.

Con./( $v, J$ )	(2, 4) $\rightarrow$ (0, 2)	(1, 0) $\rightarrow$ (0, 0)	(1, 2) $\rightarrow$ (0, 2)	References
$E^{(2)}$	6 241.120 920(1)	2 993.614 856 52(4)	2 987.291 387 6(2)	[93], [47], [47]
$E^{(4)}$	0.040 174	0.017 732	0.017 498	[44]+[23]+[47]
$E^{(5)}$	-0.033 167(25)	-0.015 397(11)	-0.015 331(11)	[23]+[21]+[22]
$E^{(6)}$	-0.000 297(1)	-0.000 138	-0.000 137	[22]+[23]
$E^{(7)}$	0.000 016(4)	0.000 007(2)	0.000 007(2)	[23]
$E_{\text{FS}}$	-0.000 031	-0.000 015	-0.000 015	[23]
Total	6 241.127 615(25)	2 993.617 047(12)	2 987.293 410(12)	
Exp.	6 241.127 647(11)	2 993.617 06(15)	2 987.293 52(15)	[93], [86], [86]
Diff.	-0.000 032(27)	-0.000 01(15)	-0.000 11(15)	

Table 6.7: Contributions to selected transitions in DT (in  $\text{cm}^{-1}$ ), in comparison to experimental values.

Con./( $v, J$ )	(1, 0) $\rightarrow$ (0, 0)	(1, 1) $\rightarrow$ (0, 1)	(1, 2) $\rightarrow$ (0, 2)	References
$E^{(2)}$	2 743.339 59(11)	2 741.729 99(11)	2 738.514 95(11)	[40]+[41]
$E^{(4)}$	0.016 399	0.016 340	0.016 221	[44]+[23]+[47]
$E^{(5)}$	-0.014 122(10)	-0.014 105(10)	-0.014 072(10)	[23]+[21]+[22]
$E^{(6)}$	-0.000 126	-0.000 126	-0.000 126	[22]+[23]
$E^{(7)}$	0.000 007(2)	0.000 007(2)	0.000 007(2)	[23]
$E_{\text{FS}}$	-0.000 011	-0.000 011	-0.000 011	[23]
Total	2 743.341 74(11)	2 741.732 09(11)	2 738.516 97(11)	
Exp.	2 743.341 71(40)	2 741.731 90(33)	2 738.516 59(40)	[94]
Diff.	+0.000 03(41)	+0.000 19(35)	+0.000 38(41)	
Con./( $v, J$ )	(1, 3) $\rightarrow$ (0, 3)	(1, 4) $\rightarrow$ (0, 4)	(1, 5) $\rightarrow$ (0, 5)	References
$E^{(2)}$	2 733.702 77(11)	2 727.305 83(11)	2 719.340 50(11)	[40]+[41]
$E^{(4)}$	0.016 043	0.015 807	0.015 514	[44]+[23]+[47]
$E^{(5)}$	-0.014 021(10)	-0.013 955(10)	-0.013 873(10)	[23]+[21]+[22]
$E^{(6)}$	-0.000 126	-0.000 125	-0.000 124	[22]+[23]
$E^{(7)}$	0.000 007(2)	0.000 007(2)	0.000 007(2)	[23]
$E_{\text{FS}}$	-0.000 011	-0.000 011	-0.000 011	[23]
Total	2 733.704 66(11)	2 727.307 55(11)	2 719.342 02(11)	
Exp.	2 733.704 70(40)	2 727.307 34(40)	2 719.341 93(40)	[94]
Diff.	-0.000 04(41)	+0.000 21(41)	+0.000 09(41)	



Table 6.8: Contributions to selected transitions in  $T_2$  (in  $\text{cm}^{-1}$ ), in comparison to experimental values.

Con./( $v, J$ )	(1, 0) $\rightarrow$ (0, 0)	(1, 1) $\rightarrow$ (0, 1)	(1, 2) $\rightarrow$ (0, 2)	References
$E^{(2)}$	2 464.502 084(61)	2 463.346 322(61)	2 461.037 196(61)	[40]
$E^{(4)}$	0.014 880	0.014 837	0.014 752	[44]+[23]+[47]
$E^{(5)}$	-0.012 699(8)	-0.012 687(8)	-0.012 662(8)	[23]+[21]+[22]
$E^{(6)}$	-0.000 114	-0.000 113	-0.000 113	[22]+[23]
$E^{(7)}$	0.000 006(2)	0.000 006(2)	0.000 006(2)	[23]
$E_{\text{FS}}$	-0.000 008	-0.000 008	-0.000 008	[23]
Total	2 464.504 150(62)	2 463.348 358(62)	2 461.039 171(62)	
Exp.	2 464.505 2(4)	2 463.349 4(3)	2 461.038 8(4)	[95]
Diff.	-0.001 1(4)	-0.001 0(3)	+0.000 4(4)	
Con./( $v, J$ )	(1, 3) $\rightarrow$ (0, 3)	(1, 4) $\rightarrow$ (0, 4)	(1, 5) $\rightarrow$ (0, 5)	References
$E^{(2)}$	2 457.579 491(61)	2 452.980 350(61)	2 447.249 243(61)	[40]
$E^{(4)}$	0.014 625	0.014 455	0.014 245	[44]+[23]+[47]
$E^{(5)}$	-0.012 626(8)	-0.012 579(8)	-0.012 519(8)	[23]+[21]+[22]
$E^{(6)}$	-0.000 113	-0.000 113	-0.000 112	[22]+[23]
$E^{(7)}$	0.000 006(2)	0.000 006(2)	0.000 006(2)	[23]
$E_{\text{FS}}$	-0.000 008	-0.000 008	-0.000 008	[23]
Total	2 457.581 374(62)	2 452.982 112(61)	2 447.250 855(61)	
Exp.	2 457.580 3(4)	2 452.981 7(4)	2 447.251 0(4)	[95]
Diff.	+0.001 1(4)	+0.000 4(4)	-0.000 1(4)	



## Summary and conclusions

The calculation of the relativistic nonadiabatic correction removes the current largest source of theory-experiment discrepancies, restoring the cohesion in the field, and yet again ensuring us of the correctness of the NRQED/NAPT approach to small molecular systems. Additionally, it is an important step on the path leading to the estimation of the proton charge radius from hydrogen molecule data. The published results have already raised much interest in the community of spectroscopists. Fortunately, thanks to the versatility of the NAPT approach, and the `H2spectr` program developed by us, the potential  $\mathcal{E}^{(4,1)}(R)$  calculated in this project can be reused to quickly obtain any other rovibrational level energies in  $\text{H}_2$  isotopomers in the ground electronic state. It constitutes a foothold for the future theory expansion because any additional calculated NRQED/NAPT contributions can be seamlessly incorporated into the code.

However, some of the theory-experiment discrepancies still remain, which is interesting to investigate. With the results presented in the thesis, it is now more likely that the source of at least some of the discrepancies lies on the experimental side. Probably the most striking example is in the dissociation energy of HD (Table 6.3) – which suspiciously breaks the trend constituted by the dissociation energies of  $\text{H}_2$  and  $\text{D}_2$ . At the same time – due to the theoretical estimates of the energy levels being calculated from the same potentials – any possible theoretical errors should express definitely more uniformly than that, leading us to believe that the source of this disagreement is experimental. Even though the experiments to which we usually compare our results are performed meticulously and with state-of-art setups, they are still subjected to errors – of both systematic and statistical nature. A notable example is the line shape model used to locate the centre of the measured peak corresponding to the transition. Thus it harks back to the case of Herzberg, Kolos, and Wolniewicz, mentioned in the Introduction – it is not only the experiment that can falsify the theory, but also the theory can help expose an error in the experiment.

Of course, there is a possibility that some of the discrepancies stem from the wrong estimation of the theoretical error. Moreover, for some transitions, e.g.  $(2, 4) \rightarrow (0, 2)$  for  $D_2$  (Table 6.6) or  $(1, 6) \rightarrow (0, 6)$  for DT (Ref. [94], not included in the tables), the experiment-theory difference is just a little bit bigger than the estimated uncertainty ( $\sigma - 1.5\sigma$ ), which is maybe not a plain disagreement, but a vague situation nevertheless, which would be valuable to resolve ultimately. To definitely disqualify the possibility of the theory being the source of the remaining discrepancies, further progress is needed, most notably in the form of inclusion of the nonadiabatic QED  $E^{(5,1)}$  corrections – to eliminate any possible source of theoretical error on this  $\alpha^n m$  level. The other – more straightforward but time consuming nonetheless – direction is calculating the fully nonadiabatic nonrelativistic  $E^{(2)}$  energies for all the rovibrational levels, which would remove the substantial error introduced to them by neglect of the higher  $m/\mu_n$  orders. Finally, in the further, long-term perspective,  $E^{(7)}$  and  $E^{(6,1)}$  contributions should be calculated too. Their inclusion should refine the theoretical estimations of the energy levels of  $H_2$  isotopomers to a quality sufficient to calculate the proton charge radius from Eq. (1.1), practically bringing this research program to a conclusion.

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# Appendices

## 8.1 Appendix A – Derivation of regularised operators

A regularisation technique [23, 54, 55] was used in Chapter 4 to remove singular operators from the expressions for the nonadiabatic relativistic correction. It relies on a known relation involving the Dirac  $\delta$ s

$$4\pi\delta^3(r_{ij}) = -\vec{\nabla}_i^2 \left( \frac{1}{r_{ij}} \right) = -\vec{\nabla}_j^2 \left( \frac{1}{r_{ij}} \right), \quad (8.1)$$

where  $\vec{\nabla}_i$  is a gradient over the coordinates of the  $i$ -th particle, and  $r_{ij} = |\vec{r}_i - \vec{r}_j|$ . For example, for the electron-nucleus delta case

$$\begin{aligned} 4\pi\delta^3(r_{1A})\psi &= -\vec{\nabla}_1^2 \left( \frac{1}{r_{1A}} \right) \psi = \vec{\nabla}_1 \frac{2}{r_{1A}} \vec{\nabla}_1 \psi - \frac{1}{r_{1A}} \vec{\nabla}_1^2 \psi - \vec{\nabla}_1^2 \frac{1}{r_{1A}} \psi \\ &= -\vec{p}_1 \frac{2}{r_{1A}} \vec{p}_1 \psi + \frac{2}{r_{1A}} \hat{T}_1 \psi + \hat{T}_1 \frac{2}{r_{1A}} \psi. \end{aligned} \quad (8.2)$$

This way the operator, the matrix element of which depends on the quality of the wave function approximation in some specific point, is expressed as a combination of operators whose expectation values depend on the wave function globally (momentum, kinetic energy). In the case of Gaussian basis functions, which are exactly that – bad at the coalescence points, good overall – it can improve the convergence dramatically (as shown in Ref. [23]). We can do even better, with the help of the following anticommutator

$$\left\{ \frac{1}{r_{1A}}, H - \mathcal{E} \right\} \psi = -\frac{2}{r_{1A}} (\mathcal{E} - V) \psi + \vec{p}_2 \frac{1}{r_{1A}} \vec{p}_2 \psi + \frac{1}{r_{1A}} \hat{T}_1 \psi + \hat{T}_1 \frac{1}{r_{1A}} \psi. \quad (8.3)$$

Hence

$$4\pi\delta^3(r_{1A})\psi = \frac{4}{r_{1A}} (\mathcal{E} - V) \psi - \vec{p}_1 \frac{2}{r_{1A}} \vec{p}_1 \psi - \vec{p}_2 \frac{2}{r_{1A}} \vec{p}_2 \psi + \left\{ \frac{2}{r_{1A}}, H - \mathcal{E} \right\} \psi, \quad (8.4)$$

or, dropping  $\psi$  altogether

$$4\pi\delta^3(r_{1A}) = \frac{4}{r_{1A}}(\mathcal{E} - V) - \vec{p}_1 \frac{2}{r_{1A}} \vec{p}_1 - \vec{p}_2 \frac{2}{r_{1A}} \vec{p}_2 + \left\{ \frac{2}{r_{1A}}, H - \mathcal{E} \right\}. \quad (8.5)$$

Note that the anticommutator vanishes when acting on  $\psi$  – the eigenfunction of  $H$  with the eigenvalue  $\mathcal{E}$  – which often makes the resulting formulas even cleaner. However, it is not always the case (which the relativistic nonadiabatic correction is a good example of), so it cannot be neglected a priori (as it was in Ref. [55]).

In the electron-electron delta case

$$4\pi\delta^3(r_{12})\psi = -\vec{\nabla}_1^2 \left( \frac{1}{r_{12}} \right) \psi = -\vec{p}_1 \frac{2}{r_{12}} \vec{p}_1 \psi + \frac{2}{r_{1A}} \hat{T}_1 \psi + \hat{T}_1 \frac{2}{r_{12}} \psi, \quad (8.6)$$

or, equivalently

$$4\pi\delta^3(r_{12})\psi = -\vec{\nabla}_2^2 \left( \frac{1}{r_{12}} \right) \psi = -\vec{p}_2 \frac{2}{r_{12}} \vec{p}_2 \psi + \frac{2}{r_{1A}} \hat{T}_2 \psi + \hat{T}_2 \frac{2}{r_{12}} \psi. \quad (8.7)$$

These two alternative formulas can be combined, together with yet another anticommutator

$$\left\{ \frac{1}{r_{12}}, H - \mathcal{E} \right\} \psi = -\frac{2}{r_{12}}(\mathcal{E} - V)\psi + \vec{p}_2 \frac{1}{r_{12}} \vec{p}_2 \psi + \frac{1}{r_{12}}(\hat{T}_1 + \hat{T}_2)\psi + (\hat{T}_1 + \hat{T}_2) \frac{1}{r_{12}} \psi. \quad (8.8)$$

Thus we obtain

$$4\pi\delta^3(r_{12}) = \frac{2}{r_{12}}(\mathcal{E} - V) - \vec{p}_1 \frac{1}{r_{12}} \vec{p}_1 - \vec{p}_2 \frac{1}{r_{12}} \vec{p}_2 + \left\{ \frac{1}{r_{12}}, H - \mathcal{E} \right\}. \quad (8.9)$$

Actually, a very similar scheme can be used to regularise the Araki-Sucher term in  $E^{(5,0)}$  (3.69)

$$P \left( \frac{1}{r_{12}^3} \right) = 2 \frac{1 + \gamma + \ln(r_{12})}{r_{12}} (\mathcal{E} - V) - p_1 \frac{\ln(r_{12})}{r_{12}} p_1 - p_2 \frac{\ln(r_{12})}{r_{12}} p_2 - (1 + \gamma) \left( p_1 \frac{1}{r_{12}} p_1 + p_2 \frac{1}{r_{12}} p_2 \right) + \left\{ \frac{1 + \gamma + \ln(r_{12})}{r_{12}}, H - \mathcal{E} \right\}, \quad (8.10)$$

$$P \left( \frac{1}{r_{aX}^3} \right) = 4 \frac{1 + \gamma + \ln(r_{aX})}{r_{aX}} (\mathcal{E} - V) - 2p_1 \frac{\ln(r_{aX})}{r_{aX}} p_1 - 2p_2 \frac{\ln(r_{aX})}{r_{aX}} p_2 - (1 + \gamma) \left( p_1 \frac{2}{r_{aX}} p_1 + p_2 \frac{2}{r_{aX}} p_2 \right) + \left\{ 2 \frac{1 + \gamma + \ln(r_{aX})}{r_{aX}}, H - \mathcal{E} \right\}. \quad (8.11)$$

The  $p_1^4 + p_2^4$  operator, present in the leading relativistic correction (the kinetic energy correction) has its regular form obtained in probably the most straightforward way of all the operators presented here

$$p_1^4 + p_2^4 = (p_1^2 + p_2^2)^2 - 2p_1^2 p_2^2 = 4(H - V)^2 - 2p_1^2 p_2^2$$

$$= 4(\mathcal{E} - V)^2 - 2p_1^2 p_2^2 + 4(H - \mathcal{E})^2 + 4\{\mathcal{E} - V, H - \mathcal{E}\}. \quad (8.12)$$

Again – the last two of the above terms can vanish if only the operator acts on  $\psi$ . However, this is not all that can be done with the  $p_1^4 + p_2^4$  operator. If  $2p_1^2 p_2^2$  acts on a wave function that fulfills the electron-electron Kato’s cusp condition, it produces a  $\delta^3(r_{12})$ -proportional term

$$2p_1^2 p_2^2 (1 + r_{12}/2)\psi = 2\tilde{p}_1^2 \tilde{p}_2^2 \psi - 8\pi\delta^3(r_{12})\psi. \quad (8.13)$$

The new  $\tilde{p}_1, \tilde{p}_2$  operators differentiate  $\psi$  ‘naively’ – as a function, not as a distribution, like  $p_1, p_2$  used to. Finally

$$p_1^4 + p_2^4 = 4(\mathcal{E} - V)^2 - 2\tilde{p}_1^2 \tilde{p}_2^2 - 8\pi\delta^3(r_{12}) + 4(H - \mathcal{E})^2 + 4\{\mathcal{E} - V, H - \mathcal{E}\}. \quad (8.14)$$

It may not be evident at the first glance, but this form of the operator is astoundingly better than the previous one, at least when calculating the relativistic  $E^{(4,0)}$  and  $E^{(4,1)}$  corrections. This is because the Dirac  $\delta$  term *exactly* cancels out with the identical term from the Darwin correction, completely removing the necessity of calculating the electron-electron delta. That is why this type of regularisation was used in Refs [23, 47] – to the great benefit of much better convergence.

## 8.2 Appendix B – Fortran codes

The `h2spectr` program was described in detail in Chapter 6. Its code is provided on the attached CD. Its contents are the following:

- `h2spectr_level.f90` – the main subroutine `level`,
- `h2spectr_types.f90` – derived types used by the program (output and potentials),
- `h2spectre.f90` – the frontend program,
- `h2spectr_presentation1.f90` – a simple example of the most basic program usage,
- `h2spectr_presentation2.f90` – an example showing the contents of the output derived type,
- `h2spectr_presentation3.f90` – an extensive presentation of calculation of rovibrational levels, all energies calculated with NAPT,
- `data/h2spectr_pot.f90` – analytic fits currently available, as well as the subroutines loading the potentials from external files,
- `data/<isotomer>.dat` – fully nonadiabatic energies of rovibrational levels of hydrogen isotopomers (in a ‘`qv qj E2full[a.u.]`’ format),
- `data/delta_ia.dat` – electron-nucleus Dirac delta potential  $\langle \psi | \sum_{a,N} \delta^3(r_{aN}) | \psi \rangle (R)$  (for the  $E^{(7)}$  (3.76) and  $E_{FS}$  (3.79) corrections),
- `data/ma4.dat` – the relativistic BO potential  $\mathcal{E}^{(4,0)}(R)$  (3.52),
- `data/ma4na.dat` – the relativistic nonadiabatic potential  $2\mu_n \mathcal{E}^{(4,1)}(R)$  (3.64),
- `data/ma5.dat` – the leading QED potential  $\mathcal{E}^{(5,0)}(R)$  (3.68),
- `data/ma6.dat` – the HQED potential  $\mathcal{E}^{(6,0)}(R)$  (3.72),
- `lapack/` – LAPACK [77] procedures,
- `pppack/` – PPPACK [75] procedures,
- `Makefile`,
- `README`.

The output of `h2spectr_presentation3.f90` (with `N=200`, `ran=10.0`) is printed below.

Working...

D0

Contr.	D0(H2)	err	D0(HD)	err	D0(D2)	err
E2	36118.79767500	0.48E-03	36406.51067624	0.27E-03	36749.09097810	0.86E-04
E4	-0.53121201	0.24E-05	-0.52988740	0.16E-05	-0.52820756	0.12E-05
E5	-0.19502104	0.23E-03	-0.19652504	0.19E-03	-0.19831434	0.15E-03
E6	-0.00205768	0.64E-05	-0.00207113	0.63E-05	-0.00208711	0.62E-05
E7	0.00010104	0.25E-04	0.00010176	0.25E-04	0.00010262	0.26E-04
Efs	-0.00003106	0.44E-07	-0.00011578	0.99E-07	-0.00020198	0.12E-06
Total	36118.06945425	0.53E-03	36405.78217865	0.33E-03	36748.36226974	0.17E-03
Exp.	36118.06962000	0.37E-03	36405.78366000	0.36E-03	36748.36286000	0.68E-03

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H2	Contr.	(0,1)	err	(3,5)->(0,3)	err	(1,0)->(0,0)	err
E2	36000.	31241313	0.49E-03	12559.75002025	0.25E-02	4161.16416907	0.91E-03
E4	-0.53379556		0.24E-05	0.06587759	0.59E-06	0.02355395	0.18E-06
E5	-0.19399830		0.23E-03	-0.06581135	0.79E-04	-0.02131734	0.26E-04
E6	-0.00204882		0.64E-05	-0.00059490	0.19E-05	-0.00019126	0.60E-06
E7	0.00010055		0.25E-04	0.00003188	0.80E-05	0.00001028	0.26E-05
Efs	-0.00003091		0.44E-07	-0.00000980	0.14E-07	-0.00000316	0.45E-08
Total	35999.58264009		0.54E-03	12559.74951367	0.25E-02	4161.16622154	0.91E-03
Exp.	35999.58283400		0.11E-04	12559.74952000	0.50E-04	4161.16636000	0.15E-03

H2 cont.	Contr.	(0,1)->(0,0)	err	(1,1)->(0,1)	err	(1,2)->(0,2)	err
E2	118.485261878		0.72E-05	4155.25196733	0.91E-03	4143.46381287	0.91E-03
E4	0.002583556		0.62E-08	0.02333327	0.18E-06	0.02289410	0.18E-06
E5	-0.001022740		0.12E-05	-0.02125626	0.26E-04	-0.02113481	0.25E-04
E6	-0.000008866		0.28E-07	-0.00019076	0.59E-06	-0.00018977	0.59E-06
E7	0.000000490		0.12E-06	0.00001025	0.26E-05	0.00001020	0.25E-05
Efs	-0.000000151		0.22E-09	-0.00000315	0.45E-08	-0.00000313	0.45E-08
Total	118.486814168		0.73E-05	4155.25386068	0.91E-03	4143.46538945	0.91E-03
Exp.	118.486800000		0.10E-03	4155.25400000	0.21E-03	4143.46553000	0.15E-03

H2 cont.	Contr.	(11,1)->(0,0)	err	(11,3)->(0,0)	err	(11,4)->(0,0)	err
E2	32938.03772658		0.48E-02	33186.77520020	0.47E-02	33380.40251961	0.47E-02
E4	-0.11936160		0.21E-05	-0.12382926	0.21E-05	-0.12777616	0.21E-05
E5	-0.16696913		0.20E-03	-0.16911765	0.20E-03	-0.17077294	0.21E-03
E6	-0.00162374		0.50E-05	-0.00164672	0.51E-05	-0.00166465	0.52E-05
E7	0.00008334		0.21E-04	0.00008446	0.21E-04	0.00008532	0.21E-04
Efs	-0.00002562		0.37E-07	-0.00002596	0.37E-07	-0.00002623	0.38E-07
Total	32937.74982983		0.48E-02	33186.48066507	0.47E-02	33380.10236495	0.47E-02
Exp.	32937.75540000		0.16E-02	33186.47910000	0.16E-02	33380.10250000	0.33E-02

HD	Contr.	(1,0)->(0,0)	err	(0,1)->(0,0)	err	(1,1)->(0,1)	err
E2	3632.15825986		0.51E-03	89.226760881	0.64E-05	3628.30233482	0.51E-03
E4	0.02099924		0.98E-07	0.001950561	0.41E-08	0.02085578	0.98E-07
E5	-0.01864085		0.18E-04	-0.000770930	0.74E-06	-0.01860085	0.18E-04
E6	-0.00016707		0.51E-06	-0.000006682	0.20E-07	-0.00016675	0.51E-06
E7	0.00000899		0.22E-05	0.000000370	0.92E-07	0.00000897	0.22E-05
Efs	-0.00001023		0.87E-08	-0.000000421	0.36E-09	-0.00001020	0.87E-08
Total	3632.16044994		0.51E-03	89.227933780	0.64E-05	3628.30442177	0.51E-03
Exp.	3632.16052000		0.22E-03	89.227931600	0.80E-06	3628.30450000	0.22E-03

HD cont.	Contr.	(2,2)->(0,1)	err	(2,3)->(0,2)	err	(2,4)->(0,3)	err
E2	7241.84625575		0.99E-03	7306.47964183	0.99E-03	7361.89937200	0.10E-02
E4	0.04092698		0.20E-06	0.04192720	0.20E-06	0.04255918	0.20E-06
E5	-0.03746091		0.36E-04	-0.03797164	0.37E-04	-0.03838095	0.37E-04
E6	-0.00033661		0.10E-05	-0.00034116	0.10E-05	-0.00034487	0.10E-05
E7	0.00001809		0.45E-05	0.00001834	0.46E-05	0.00001854	0.46E-05
Efs	-0.00002058		0.18E-07	-0.00002086	0.18E-07	-0.00002109	0.18E-07
Total	7241.84938272		0.99E-03	7306.48325370	0.10E-02	7361.90320280	0.10E-02
Exp.	7241.84935616		0.67E-06	7306.48322784	0.93E-06	7361.90317873	0.93E-06

D2						
Contr.	(2,4)->(0,2)	err	(1,0)->(0,0)	err	(1,2)->(0,2)	err
E2	6241.12095459	0.32E-03	2993.61487692	0.17E-03	2987.29140774	0.17E-03
E4	0.04017379	0.11E-06	0.01773208	0.48E-07	0.01749787	0.48E-07
E5	-0.03316684	0.25E-04	-0.01539690	0.11E-04	-0.01533107	0.11E-04
E6	-0.00029695	0.88E-06	-0.00013784	0.41E-06	-0.00013730	0.41E-06
E7	0.00001600	0.40E-05	0.00000742	0.19E-05	0.00000739	0.18E-05
Efs	-0.00003149	0.18E-07	-0.00001460	0.85E-08	-0.00001454	0.85E-08
Total	6241.12764911	0.33E-03	2993.61706708	0.17E-03	2987.29343009	0.17E-03
Exp.	6241.12764700	0.11E-04	2993.61706000	0.15E-03	2987.29352000	0.15E-03

DT						
Contr.	(1,0)->(0,0)	err	(1,1)->(0,1)	err	(1,2)->(0,2)	err
E2	2743.33959152	0.11E-03	2741.72998945	0.11E-03	2738.51494815	0.11E-03
E4	0.01639918	0.39E-07	0.01633961	0.39E-07	0.01622072	0.38E-07
E5	-0.01412188	0.96E-05	-0.01410508	0.96E-05	-0.01407156	0.96E-05
E6	-0.00012637	0.37E-06	-0.00012623	0.37E-06	-0.00012595	0.37E-06
E7	0.00000680	0.17E-05	0.00000680	0.17E-05	0.00000678	0.17E-05
Efs	-0.00001127	0.19E-06	-0.00001126	0.19E-06	-0.00001123	0.19E-06
Total	2743.34173799	0.11E-03	2741.73209329	0.11E-03	2738.51696691	0.11E-03
Exp.	2743.34171000	0.40E-03	2741.73190000	0.32E-03	2738.51659000	0.40E-03

DT cont.						
Contr.	(1,3)->(0,3)	err	(1,4)->(0,4)	err	(1,5)->(0,5)	err
E2	2733.70276667	0.11E-03	2727.30582594	0.11E-03	2719.34050492	0.11E-03
E4	0.01604301	0.38E-07	0.01580723	0.38E-07	0.01551435	0.37E-07
E5	-0.01402149	0.96E-05	-0.01395511	0.95E-05	-0.01387276	0.95E-05
E6	-0.00012554	0.37E-06	-0.00012500	0.37E-06	-0.00012432	0.37E-06
E7	0.00000676	0.17E-05	0.00000673	0.17E-05	0.00000669	0.17E-05
Efs	-0.00001119	0.19E-06	-0.00001114	0.19E-06	-0.00001108	0.19E-06
Total	2733.70465822	0.11E-03	2727.30754865	0.11E-03	2719.34201780	0.11E-03
Exp.	2733.70470000	0.40E-03	2727.30734000	0.40E-03	2719.34193000	0.40E-03

T2						
Contr.	(1,0)->(0,0)	err	(1,1)->(0,1)	err	(1,2)->(0,2)	err
E2	2464.50208431	0.61E-04	2463.34632235	0.61E-04	2461.03719645	0.61E-04
E4	0.01488016	0.32E-07	0.01483745	0.32E-07	0.01475218	0.31E-07
E5	-0.01269869	0.80E-05	-0.01268660	0.79E-05	-0.01266248	0.79E-05
E6	-0.00011358	0.33E-06	-0.00011348	0.33E-06	-0.00011328	0.33E-06
E7	0.00000612	0.15E-05	0.00000611	0.15E-05	0.00000610	0.15E-05
Efs	-0.00000823	0.34E-06	-0.00000822	0.34E-06	-0.00000821	0.34E-06
Total	2464.50415010	0.62E-04	2463.34835761	0.62E-04	2461.03917077	0.62E-04
Exp.	2464.50520000	0.40E-03	2463.34940000	0.30E-03	2461.03880000	0.40E-03

T2 cont.						
Contr.	(1,3)->(0,3)	err	(1,4)->(0,4)	err	(1,5)->(0,5)	err
E2	2457.57949056	0.61E-04	2452.98034994	0.61E-04	2447.24924340	0.61E-04
E4	0.01462463	0.31E-07	0.01445524	0.31E-07	0.01424457	0.31E-07
E5	-0.01262640	0.79E-05	-0.01257853	0.79E-05	-0.01251905	0.78E-05
E6	-0.00011298	0.33E-06	-0.00011259	0.33E-06	-0.00011210	0.33E-06
E7	0.00000608	0.15E-05	0.00000606	0.15E-05	0.00000603	0.15E-05
Efs	-0.00000818	0.34E-06	-0.00000815	0.34E-06	-0.00000812	0.33E-06
Total	2457.58137371	0.62E-04	2452.98211197	0.61E-04	2447.25085474	0.61E-04
Exp.	2457.58030000	0.40E-03	2452.98170000	0.40E-03	2447.25100000	0.40E-03

```
real    0m3.878s
user    0m3.875s
sys     0m0.000s
```

All the sources of the experimental data cited here are provided in Tables 6.3–6.8. The timing was obtained with the Bash `time` command on a GNU/Linux system with an Intel(R) Xeon(R) CPU E5-1620 v3 @ 3.50GHz processor. The code should potentially be trivial to parallelise – because the level energies are calculated independently. However, with such a short execution time, it is pointless for our purposes. Compared to the results presented in Chapter 6, all of the above results are obtained with NAPT – they do not contain fully nonadiabatic results for  $E^{(2)}$  and  $E^{(5)}$ , present in Tables 6.3–6.8. Furthermore, the  $E^{(4)}$  contributions are calculated with the potential obtained in the largest basis set (512), without the extrapolation to the complete basis set limit.

*Second version note: The CD is not included in this version of the thesis. If you are interested in H2spectr, please feel free to contact the author of the thesis (pczachor1@gmail.com) for the recent version.*

### 8.3 Appendix C – ECE functions: auxiliary expressions

The  $R$  expansion terms of the inhomogeneous term (5.16), shown in this Appendix, have been already provided in my MSc thesis [64]. The small- $t$ -case terms, however, are my new result and I have decided to gather all of them in one place – here.

#### General case

The recurrence relations (5.19, 5.20) for the master integral (5.5) for explicitly correlated exponential functions depend on the expansion terms of the inhomogeneous term  $F$  (5.16). It is noteworthy that the exponential integral  $\text{Ei}(x)$  function, which it contains, has a singularity of a logarithmic type in  $x = 0$ . Fortunately, it can be extracted by introducing a new function,  $\text{EEi}$ :

$$\text{EEi}(x) = \text{Ei}(x) - \ln|x| - \gamma_E, \quad (8.15)$$

where  $\gamma_E \approx 0.5772\dots$  is the Euler-Mascheroni constant. Moreover, it can be shown [64], that it is convenient to slightly redefine the expansion series (5.12)

$$f_n = f_n^{(1)} \left[ \frac{1}{2} \ln(R^2(t+2u)(t+2w)) + \gamma_E \right] + f_n^{(2)}, \quad (8.16)$$

and the corresponding inhomogeneous term definition. It causes some of the terms provided below to be nonzero for even or odd values of  $n$  only. At the same time, the recurrence relations (5.19, 5.20) retain their form provided in Chapter 5 – only the leading terms change.

Then, the expressions for the logarithmic  $F^{(1)}$  and non-logarithmic  $F^{(2)}$  parts (5.21) are the following [64]

$$F_n^{(1)} = \left\{ \begin{array}{ll} -2[p_1 D_1(n) + p_2 D_2(n) + p_3 D_3(n) + p_4 D_4(n)], & n \in \text{Odd} \\ 0, & n \in \text{Even} \end{array} \right\}, \quad (8.17)$$

$$F_n^{(2)} = F_n^{(2A)} + F_n^{(2B)}, \quad (8.18)$$

$$F_n^{(2A)} = \left\{ \begin{array}{ll} -[p_1 D_1(n) + p_2 D_2(n) - p_3 D_3(n) - p_4 D_4(n)] \ln \left[ \frac{t+2u}{2(u+w)} \right] \\ -[p_1 D_1(n) + p_2 D_2(n) + p_3 D_3(n) + p_4 D_4(n)] \ln \left[ \frac{t+2u}{2(u+w)} \right], & n \in \text{Even} \\ 0, & n \in \text{Odd} \end{array} \right\}, \quad (8.19)$$

$$\begin{aligned} F_n^{(2B)} &= [D_1(n+2) + D_2(n+2) - D_5(n+2) - D_6(n+2)](n+1)t \\ &+ [D_5(n+1) + D_6(n+1)]t^2 \\ &+ p_1 [-\text{Fe}_n(-d_1, -(t-2x)) - \text{Fe}_n(-d_1, -(t-2y))] \end{aligned}$$

$$\begin{aligned}
& + \text{Fe}_n(-d_1, 2(x+y)) + \text{Fe}_n(d_1, -2(u+w))] \\
& + p_2 [-\text{Fe}_n(-d_2, -(t+2y)) - \text{Fe}_n(-d_2, -(t+2x)) \\
& + \text{Fe}_n(-d_2, -2(x+y)) + \text{Fe}_n(d_2, -2(u+w))] \\
& + p_3 [\text{Fe}_n(d_3, -(t+2u)) - \text{Fe}_n(-d_3, -(t+2w))] \\
& + p_4 [\text{Fe}_n(d_4, -(t+2u)) - \text{Fe}_n(-d_4, -(t+2w))], \tag{8.20}
\end{aligned}$$

where

$$p_1 = 2(uwx + uw y + ux y + wx y) + \frac{t^2 d_1}{2}, \tag{8.21}$$

$$p_2 = 2(-uw x - uw y + ux y + wx y) + \frac{t^2 d_2}{2}, \tag{8.22}$$

$$p_3 = 2(-uw x + uw y - ux y + wx y) + \frac{t^2 d_3}{2}, \tag{8.23}$$

$$p_4 = 2(uwx - uw y - ux y + wx y) + \frac{t^2 d_4}{2}, \tag{8.24}$$

and where

$$d_1 = u + w + x + y, \tag{8.25}$$

$$d_2 = u + w - x - y, \tag{8.26}$$

$$d_3 = u - w + x - y, \tag{8.27}$$

$$d_4 = u - w - x + y, \tag{8.28}$$

$$d_5 = u + w + x - y + t, \tag{8.29}$$

$$d_6 = u + w - x + y + t, \tag{8.30}$$

$$D_i(n) = \frac{(-d_i)^n}{n!}. \tag{8.31}$$

The above formula contains a lot of expressions of the type:

$$\text{Fe}_n(a, b) = \left\{ \begin{array}{ll} \frac{a \text{Fe}_{n-1}(a, b)}{n} + \frac{(a+b)^n - a^n}{nn!}, & \text{for } n > 0 \\ 0, & \text{otherwise} \end{array} \right\}. \tag{8.32}$$

They are the expansion terms of

$$\text{Fe}(a, b) = e^{ar} \text{EEi}(br) = \sum_{n=0}^{\infty} \text{Fe}_n(a, b) R^n. \tag{8.33}$$

The recurrence relations (5.19, 5.20) need terms from which they could start. The leading one can be found by considering a helium-type integral [62]

$$f_1 R = R \lim_{R \rightarrow 0} \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-tr_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})}}{r_{12} r_{1A} r_{1B} r_{2A} r_{2B}}, \tag{8.34}$$

$$\begin{aligned}
f_1 &= \lim_{R \rightarrow 0} \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-tr_{12} - u(r_{1A} + r_{1B}) - w(r_{2A} + r_{2B}) - y(r_{1A} - r_{1B}) - x(r_{2A} - r_{2B})}}{r_{12} r_{1A} r_{1B} r_{2A} r_{2B}} \\
&= \int \frac{d^3 r_1}{4\pi} \int \frac{d^3 r_2}{4\pi} \frac{e^{-tr_{12} - 2ur_{1A} - 2wr_{2A}}}{r_{12} r_{1A}^2 r_{2A}^2} \\
&= \frac{1}{2t} \left[ \frac{\pi^2}{6} + \frac{1}{2} \ln^2 \left( \frac{2u+t}{2w+t} \right) + \text{Li}_2 \left( 1 - \frac{2(u+w)}{2u+t} \right) + \text{Li}_2 \left( 1 - \frac{2(u+w)}{2w+t} \right) \right], \quad (8.35)
\end{aligned}$$

where  $\text{Li}_2$  is a dilogarithm

$$\text{Li}_2(z) = \sum_{n=1}^{\infty} \frac{z^n}{n^2}.$$

It means that  $f_1^{(1)} = 0$ ,  $f_1^{(2)} = f_1$ . Moreover,  $f_0^{(i)} = f_{-1}^{(i)} = 0$  [62]. The rest of the required starting terms can be calculated from the four-body lithium integral expansion terms [65]

$$f_2^{(1)} = 1, \quad (8.36)$$

$$f_2^{(2)} = -3/2. \quad (8.37)$$

### Small $t$ case

For the small  $t$  expansion, the expressions are analogous

$$F_{n,m}^{(1)} = \begin{cases} (n+1)(D_1(n+1) + D_2(n+1) + D_3(n+1) + D_4(n+1)), & n \in \text{Odd}, \quad m = 2, \\ 0, & \text{Otherwise} \end{cases}, \quad (8.38)$$

$$F_{n,m}^{(2)} = F_{n,m}^{(2A)} + F_{n,m}^{(2B)}, \quad (8.39)$$

$$F_{n,m}^{(2A)} = \begin{cases} \left. \begin{aligned} &\Lambda_1(m)q_1 D_1(n) - \frac{1}{2}(n+1)\Lambda_1(m-2)D_1(n+1) + \Lambda_1(m)q_2 D_2(n) \\ &- \frac{1}{2}(n+1)\Lambda_1(m-2)D_2(n+1) + \Lambda_2(m)q_3 D_3(n) \\ &- \frac{1}{2}(n+1)\Lambda_2(m-2)D_3(n+1) \\ &+ \Lambda_2(m)q_4 D_4(n) - \frac{1}{2}(n+1)\Lambda_2(m-2)D_4(n+1), \end{aligned} \right\} n \in \text{Even}, \\ 0, & n \in \text{Odd} \end{cases}, \quad (8.40)$$

$$\begin{aligned}
F_{n,m}^{(2B)} &= d_3 \frac{1}{2} (-\text{Fe}_{n,m-2}(-d_3, 2x, -1) - \text{Fe}_{n,m-2}(-d_3, 2y, -1) \\
&\quad + \text{Fe}_{n,m-2}(-d_3, 2(x+y), 0) + \text{Fe}_{n,m-2}(d_3, -2(u+w), 0)) \\
&\quad + d_4 \frac{1}{2} (-\text{Fe}_{n,m-2}(-d_4, -2y, -1) - \text{Fe}_{n,m-2}(-d_4, -2x, -1) \\
&\quad + \text{Fe}_{n,m-2}(-d_4, -2(x+y), 0) + \text{Fe}_{n,m-2}(d_4, -2(u+w), 0)) \\
&\quad + d_1 \frac{1}{2} (\text{Fe}_{n,m-2}(d_1, -2u, -1) - \text{Fe}_{n,m-2}(-d_1, -2w, -1))
\end{aligned}$$

$$\begin{aligned}
& + d_2 \frac{1}{2} (\text{Fe}_{n,m-2}(d_2, -2u, -1) - \text{Fe}_{n,m-2}(-d_2, -2w, -1)) \\
& + (\text{Fe}_{n,m}(d_1, -2u, -1) - \text{Fe}_{n,m}(-d_1, -2w, -1))q_1 \\
& + (\text{Fe}_{n,m}(d_2, -2u, -1) - \text{Fe}_{n,m}(-d_2, -2w, -1))q_2 \\
& + (-\text{Fe}_{n,m}(-d_3, 2x, -1) - \text{Fe}_{n,m}(-d_3, 2y, -1)) \\
& + \text{Fe}_{n,m}(-d_3, 2(x+y), 0) + \text{Fe}_{n,m}(d_3, -2(u+w), 0)q_3 \\
& + (-\text{Fe}_{n,m}(-d_4, -2y, -1) - \text{Fe}_{n,m}(-d_4, -2x, -1)) \\
& + \text{Fe}_{n,m}(-d_4, -2(x+y), 0) + \text{Fe}_{n,m}(d_4, -2(u+w), 0)q_4 \\
& + Q_5(n+1, m-2) + Q_6(n+1, m-2) \\
& + (n+1)(-Q_5(n+2, m-1) - Q_6(n+2, m-1)), \tag{8.41}
\end{aligned}$$

where

$$Q_5(n, m) = \frac{(-q_5)^{n-m}}{m!(n-m)!}, \tag{8.42}$$

$$Q_6(n, m) = \frac{(-q_6)^{n-m}}{m!(n-m)!}, \tag{8.43}$$

and where

$$q_1 = -2u w x + 2u w y - 2u x y + 2w x y, \tag{8.44}$$

$$q_2 = 2u w x - 2u w y - 2u x y + 2w x y, \tag{8.45}$$

$$q_3 = 2u w x + 2u w y + 2u x y + 2w x y, \tag{8.46}$$

$$q_4 = -2u w x - 2u w y + 2u x y + 2w x y, \tag{8.47}$$

$$q_5 = 2u w - 2u x + 2w x, \tag{8.48}$$

$$q_6 = -2u w - 2u x + 2w x, \tag{8.49}$$

and where

$$\Lambda_1(m) = \left\{ \begin{array}{ll} \ln\left(\frac{u}{w}\right), & m = 0 \\ \frac{-(-2u)^{-m} + (-2w)^{-m}}{m}, & m > 0 \end{array} \right\}, \tag{8.50}$$

$$\Lambda_2(m) = \left\{ \begin{array}{ll} \ln\left(\frac{(u+w)^2}{u w}\right), & m = 0 \\ \frac{(-2u)^{-m} + (-2w)^{-m}}{m}, & m > 0 \end{array} \right\}. \tag{8.51}$$

The terms containing the exponential integral Ei are also expanded both in  $R$  and  $t$

$$\text{Fe}(a, b, s) = e^{ar} \text{EEi}([s t + b]r) = \sum_{n=0}^{\infty} \text{Fe}_{nm}(a, b, s) R^n t^m, \tag{8.52}$$

$$\text{Fe}_{nm}(a, b, s) = \left\{ \begin{array}{ll} \frac{1}{n} \left[ a \text{Fe}_{n-1, m} + \frac{s^m (a+b)^{n-m}}{m!(n-m)!} \right], & \text{for } n > 0, m > 0 \\ \frac{1}{n} \left[ a \text{Fe}_{n-1, 0} + \frac{(a+b)^n - a^n}{n!} \right], & \text{for } n > 0, m = 0 \\ 0, & \text{otherwise} \end{array} \right\}. \tag{8.53}$$

The leading recurrence (5.25, 5.26) terms for the small  $t$  case can be obtained simply by expansion of the general-case ones in  $t$

$$f_{1m}^{(2)} = \frac{1}{2(m+1)(2(u+w))^{m+1}} \left( \mathcal{L}_m \left( \frac{w}{u+w}, -1 \right) - \mathcal{L}_m \left( \frac{w}{u+w}, 1 \right) + \mathcal{L}_m \left( \frac{u}{u+w}, -1 \right) - \mathcal{L}_m \left( \frac{u}{u+w}, 1 \right) \right), \quad (8.54)$$

where

$$\mathcal{L}_m(a, s) = -\frac{s}{a} \left( \mathcal{L}_{m-1}(a, s) + \frac{1}{m}(a-1)^m \right), \quad (8.55)$$

$$\mathcal{L}_0(a, s) = \frac{\ln(1-a)}{s a}. \quad (8.56)$$

The other needed terms can also be easily deduced from the general case:

$$f_{20}^{(2)} = -3/2, \quad (8.57)$$

$$f_{0m}^{(i)} = f_{-1m}^{(i)} = 0, \quad (8.58)$$

$$f_{1m}^{(1)} = 0, \quad (8.59)$$

$$f_{2m}^{(1)} = \left\{ \begin{array}{ll} 1, & \text{for } m = 0 \\ 0, & \text{otherwise} \end{array} \right\}. \quad (8.60)$$



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