Finite nuclear mass corrections to electric and magnetic interactions in diatomic molecules

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Abstract

In order to interpret precise measurements of molecular properties finite nuclear mass corrections to the Born-Oppenheimer approximation have to be accounted for. It is demonstrated that they can be obtained systematically using nonadiabatic perturbation theory. The formulae for the leading corrections to the relativistic contribution to energy, the transition electric dipole moment, the electric polarizability, and the magnetic shielding constant are derived. They can be conveniently calculated for a fixed position of nuclei, as in the Born-Oppenheimer approximation, and next averaged over the rovibrational function.

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I. INTRODUCTION

In the calculation of some molecular properties, the magnetic shielding for example, one usually assumes the nuclei have fixed positions, the so called Born-Oppenheimer (BO) approximation, and at the final stage averages over the appropriate vibration-rotational wave function. The principal question we address in this work is what are the finite nuclear mass corrections to various physical properties of the molecule, such as relativistic energies, polarizabilities, or the above mentioned magnetic shielding evaluated in the BO approximation. Direct nonadiabatic calculations are possible only for small molecules and only for simple properties such as the electric dipole polarizability [1, 2]. This approach, however, is not universal, and has not yet been applied to more complex molecules such as H_2O, or to the evaluation of the nuclear spin-rotation and shielding constants. In this work we demonstrate the applicability of nonadiabatic perturbation theory (NAPT) [3] to obtain in a systematic way the formulae for various physical properties of a diatomic molecule, with possible extensions to larger molecules. We rederive the known result for the electric static polarizability, the rotational magnetic moment, and the spin-rotation constant, and obtain the leading finite nuclear mass corrections (which we will call in this work nonadiabatic corrections) to relativistic rovibrational energies, the transition electric dipole moment, the electric static polarizability, and the magnetic shielding constant. These finite nuclear mass corrections are important for comparison between accurate measurement and precise calculations, for example in the dissociation energy of H_2 [4, 5], the transition electric-dipole moment of LiH [6], or in the shielding constant of H_2 and isotopomers [7].

We demonstrate in this work that the leading finite nuclear mass corrections can be conveniently calculated for a fixed position of nuclei, as in the BO approximation, and averaged out over the rovibrational wave function. We do not consider here the second order corrections in the nuclear Hamiltonian $H_{\rm n}$, but for consistency regard them also as nonadiabatic corrections, although of higher order.

In Sec. II we define the reference frame and split the nonrelativistic Hamiltonian into electronic and nuclear parts. In Sec. III we briefly present NAPT on the basis of Ref. [3], include nonadiabatic corrections to the BO wave function, and derive general formulae for first and the second order matrix elements. In Sec. IV, as a first example, we derive formulae for relativistic recoil corrections to rovibrational energies in diatomic molecules.

Further examples are finite nuclear mass corrections to electric properties of molecules, derived in Sec. V, and to magnetic properties of molecules, derived in Sec. VI. We briefly summarize our results in Sec. VII.

II. NONRELATIVISTIC HAMILTONIAN

We consider a neutral diatomic molecule with the Hamiltonian

$$H = \sum_a \frac{\vec{p}_a^{\,2}}{2\,m} + \frac{\vec{p}_A^{\,2}}{2\,m_A} + \frac{\vec{p}_B^{\,2}}{2\,m_B} + V, \tag{1}$$

where the summation index a goes over all electrons and A and B refers to nuclei. In order to derive formulae for nonadiabatic effects, one must fix the reference frame. We start with the laboratory frame $\{\vec{R}_A,\, \vec{R}_B,\, \vec{r}_a\}$, and change variables to $\{\vec{R},\, \vec{R}_G,\, \vec{x}_a\}$ according to

$$\begin{aligned} \vec{R}_A &= \vec{R}_G + \epsilon_B\,\vec{R}, && (2)\\ \vec{R}_B &= \vec{R}_G - \epsilon_A\,\vec{R}, && (3)\\ \vec{r}_a &= \vec{R}_G + \vec{x}_a, && (4) \end{aligned}$$

with the relative position of nuclei $\vec{R} = \vec{R}_A - \vec{R}_B$, and the new frame origin, arbitrarily chosen on the molecular symmetry axis, $\vec{R}_G = \epsilon_A\,\vec{R}_A + \epsilon_B\,\vec{R}_B$, where $\epsilon_A + \epsilon_B = 1$. The conjugate momenta are related by

$$\begin{aligned} \vec{p}_A &= \epsilon_A\,\vec{P}_G + \vec{P} - \epsilon_A \sum_a \vec{q}_a, && (5)\\ \vec{p}_B &= \epsilon_B\,\vec{P}_G - \vec{P} - \epsilon_B \sum_a \vec{q}_a, && (6)\\ \vec{p}_a &= \vec{q}_a, && (7) \end{aligned}$$

where $\vec{P} = -i\,\vec{\nabla}_R$ and $\vec{q}_a = -i\,\vec{\nabla}_{x_a}$. The nonrelativistic wave function with vanishing total momentum does not depend on $\vec{R}_G$, so $\phi = \phi(\vec{x}_a,\, \vec{R})$, and since $\vec{P}_G$ commutes with H when expressed in the new variables, it can be set to 0. The Hamiltonian H in the new variables becomes

$$\begin{aligned} H = {} & \sum_a \frac{\vec{q}_a^{\,2}}{2\,m} + V + \left(\frac{1}{2\,m_A} + \frac{1}{2\,m_B}\right) \vec{P}^{\,2} + \left(\frac{\epsilon_A^2}{2\,m_A} + \frac{\epsilon_B^2}{2\,m_B}\right) \Big(\sum_a \vec{q}_a\Big)^2 \\ & - \left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) \vec{P} \cdot \sum_a \vec{q}_a. \end{aligned} \tag{8}$$

The last term in the above is transformed by the unitary transformation

$$\tilde{H} = e^{-i\,\varphi}\, H\, e^{i\,\varphi} = H - i[\varphi\;,\; H] + \ldots \tag{9}$$

where

$$\varphi = m\left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right)\sum_a \vec{x}_a \cdot \vec{P}, \tag{10}$$

and

$$e^{-i\,\varphi}\, q_a^i\, e^{i\,\varphi} = q_a^i + m\left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) P^i, \tag{11}$$

with higher order $O(m/M)^2$ terms in the electron nuclear mass ratio being neglected, with M equal to m_A or m_B. As a result of this transformation the Hamiltonian takes the form

$$\begin{aligned}
\tilde{H} &= H_{\rm el} + H_{\rm n}, && (12)\\
H_{\rm el} &= \sum_a \frac{\vec{q}_a^{\,2}}{2\,m} + V, && (13)\\
H_{\rm n} &= \left(\frac{1}{2\,m_A} + \frac{1}{2\,m_B}\right)\vec{P}^{\,2} + \left(\frac{\epsilon_A^2}{2\,m_A} + \frac{\epsilon_B^2}{2\,m_B}\right)\Big(\sum_a \vec{q}_a\Big)^2 \\
&\quad - m\left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right)\sum_a \vec{x}_a \cdot \vec{\nabla}_R(V) && (14)\\
&= H_{\rm n}' + H_{\rm n}'', && (15)
\end{aligned}$$

where $H_{\rm n}'$ includes the first term and $H_{\rm n}''$ the two remaining terms. This form of the nuclear Hamiltonian is convenient for the calculation of nonadiabatic effects. Moreover the freedom in choosing $\epsilon_{A,B}$ will be used in order to simplify formulae for nonadiabatic corrections to electric and magnetic properties. Later, we will need the angular momentum operator $\vec{J}$, which for states with vanishing total momentum is defined by

$$\vec{J} = \sum_a (\vec{r}_a - \vec{R}_{CM}) \times \vec{p}_a + (\vec{R}_A - \vec{R}_{CM}) \times \vec{p}_A + (\vec{R}_B - \vec{R}_{CM}) \times \vec{p}_B, \tag{16}$$

where $\vec{R}_{CM}$ is the molecular center of mass. In the new variables the operator $\vec{J}$

$$\vec{J} = \sum_a \vec{x}_a \times \vec{q}_a + \vec{R} \times \vec{P} \equiv \vec{J}_{\rm el} + \vec{J}_{\rm n} \tag{17}$$

is split into electronic $\vec{J}_{\rm el}$ and nuclear $\vec{J}_{\rm n}$ parts, and this $\vec{J}$ is not modified by the unitary transformation of Eq. (9).

III. NONADIABATIC PERTURBATION THEORY

The total nonrelativistic wave function ϕ of an arbitrary molecule is the solution of the stationary Schrödinger equation

$$[H - E]\,|\phi\rangle = 0\,, \tag{18}$$

with the Hamiltonian H being a sum of the electronic $H_{\rm el}$ and nuclear $H_{\rm n}$ parts, Eq. (12). In the adiabatic approximation $\phi = \phi_{\rm a}$, where

$$\phi_{\rm a}(\vec{x}, \vec{R}) = \phi_{\rm el}(\vec{x})\; \chi(\vec{R}) \tag{19}$$

is represented as a product of the electronic wave function $\phi_{\rm el}$ and the nuclear wave function χ. We note that $\phi_{\rm el}$ depends implicitly on the nuclear relative coordinate $\vec{R}$. The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

$$[H_{\rm el} - \mathcal{E}_{\rm el}(R)]\,|\phi_{\rm el}\rangle = 0, \tag{20}$$

while the nuclear wave function is a solution to the Schrödinger equation in the effective potential generated by electrons

$$[H_{\rm n} + \mathcal{E}_{\rm a}(R) + \mathcal{E}_{\rm el}(R) - E_{\rm a}]\,|\chi\rangle = 0\,, \tag{21}$$

where

$$\mathcal{E}_{\rm a}(R) = \langle\phi_{\rm el}|H_{\rm n}|\phi_{\rm el}\rangle_{\rm el}\,. \tag{22}$$

In NAPT, the total wave function

$$\phi = \phi_{\rm a} + \delta\phi_{\rm na} = \phi_{\rm el}\,\chi + \delta\phi_{\rm na} \tag{23}$$

is the sum of the adiabatic solution and a nonadiabatic correction. The nonadiabatic correction $\delta\phi_{\rm na}$ is decomposed into two parts,

$$\delta\phi_{\rm na} = \phi_{\rm el}\,\delta\chi + \delta'\phi_{\rm na}\,, \tag{24}$$

obeying the following orthogonality conditions

$$\langle\delta'\phi_{\rm na}|\phi_{\rm el}\rangle_{\rm el} \;=\; 0\,, \tag{25}$$

$$\langle\delta\chi|\chi\rangle \;=\; 0\,, \tag{26}$$

which imply the normalization condition $\langle\phi_a|\phi\rangle = 1$.

In the first order in $H_{\rm n}$ of NAPT one has

$$|\delta'\phi_{\rm na}\rangle^{(1)} \;=\; \frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}\,|\phi_{\rm el}\,\chi\rangle, \tag{27}$$

and in the second order

$$|\delta'\phi_{\rm na}\rangle^{(2)} \;=\; \frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(H_{\rm n}+\mathcal{E}_{\rm el}-E_{\rm a})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}\,|\phi_{\rm el}\,\chi\rangle, \tag{28}$$

where $1/(\mathcal{E}_{\rm el}-H_{\rm el})'$ denotes the resolvent with the reference state $\phi_{\rm el}$ subtracted out. The total nuclear function $\chi+\delta\chi$ satisfies the effective Schrödinger equation which includes adiabatic and nonadiabatic corrections [3]. Thus the nonadiabatic wave function can be recovered order by order in the perturbative approach. Eqs. (27,28) involve $H_{\rm n}$, and thus derivatives with respect to $\vec{R}$. These derivatives can be calculated with the help of the following formulae

$$\vec{\nabla}_R|\phi_{\rm el}\rangle \;=\; \frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\vec{\nabla}_R(V)|\phi_{\rm el}\rangle, \tag{29}$$

$$\begin{aligned}\vec{\nabla}_R\Big[\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\Big] \;=\;& \frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\vec{\nabla}_R(V-\mathcal{E}_{\rm el})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\\ &-\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'^2}\,\vec{\nabla}_R(V)|\phi_{\rm el}\rangle\langle\phi_{\rm el}|\\ &-|\phi_{\rm el}\rangle\langle\phi_{\rm el}|\,\vec{\nabla}_R(V)\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'^2}.\end{aligned} \tag{30}$$

It has been shown recently in [3] that the application of these formulae allows for a significant improvement in the numerical accuracy of adiabatic and nonadiabatic corrections in the H_2 molecule, and this probably will hold for any diatomic molecule. Alternatively, one may use the formula

$$\vec{\nabla}_R = \vec{n}\,(\vec{n}\cdot\vec{\nabla}_R) - \vec{n}\times(\vec{n}\times\vec{\nabla}_R), \tag{31}$$

where $\vec{n}=\vec{R}/R$, with only the first radial part in above equation replaced in terms of the derivative $\partial(V-\mathcal{E}_{\rm el})/\partial R$, namely

$$\vec{\nabla}_R|\phi_{\rm el}\rangle = \vec{n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\frac{\partial V}{\partial R}|\phi_{\rm el}\rangle - \frac{i}{R}\vec{n}\times\vec{J}_{\rm n}|\phi_{\rm el}\rangle. \tag{32}$$

For example, the adiabatic correction to energy becomes

$$\begin{aligned}\mathcal{E}_{\rm a}(R) \;=\;& \langle\phi_{\rm el}|H_{\rm n}|\phi_{\rm el}\rangle\\ =\;& \langle\phi_{\rm el}|H''_{\rm n}+\frac{\vec{J}^2_{\rm n}}{2\,m_{\rm n}\,R^2}|\phi_{\rm el}\rangle + \langle\phi_{\rm el}|\frac{\partial V}{\partial R}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'^2}\,\frac{\partial V}{\partial R}|\phi_{\rm el}\rangle,\end{aligned} \tag{33}$$

where $m_{\rm n}$ is the nuclear reduced mass and for Σ electronic state $\vec{J}_{\rm n}|\phi_{\rm el}\rangle$ can be replaced by $-\vec{J}_{\rm el}|\phi_{\rm el}\rangle$. In this way one avoids summation over intermediate states with the Π symmetry.

A. First order matrix elements

We will use here NAPT to derive the finite nuclear mass corrections to various matrix elements in a general form. Later we will analyze specific examples. Consider at first the Hermitian electronic operator Q (no derivatives with respect to nuclear variables, for example the relativistic correction to kinetic energy of electrons) and its matrix element between (different) rovibrational states. In the BO approximation this matrix element can be represented in terms of the electronic matrix element nested in the nuclear matrix element, namely

$$\langle Q\rangle^{(0)} \equiv \langle\phi_{\rm el}\,\chi_{\rm f}|Q|\phi_{\rm el}\,\chi_{\rm i}\rangle = \langle\chi_{\rm f}|\langle Q\rangle^{(0)}_{\rm el}|\chi_{\rm i}\rangle, \tag{34}$$

$$\langle Q\rangle^{(0)}_{\rm el} \equiv \langle Q\rangle_{\rm el} = \langle\phi_{\rm el}|Q|\phi_{\rm el}\rangle. \tag{35}$$

We will show that the same holds for nonadiabatic corrections to this matrix element, which are

$$\langle Q\rangle^{(1)} = \langle\phi_{\rm el}\,\chi_{\rm f}|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q|\phi_{\rm el}\,\chi_{\rm i}\rangle + \langle\phi_{\rm el}\,\chi_{\rm f}|Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}|\phi_{\rm el}\,\chi_{\rm i}\rangle. \tag{36}$$

Although in this work we consider only the first order $O(m/M)$ corrections, let us present here the second order corrections to the diagonal matrix element to demonstrate the application of NAPT

$$\begin{aligned}\langle Q\rangle^{(2)} = {} & \langle\phi_{\rm el}\,\chi|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(H_{\rm n}+\mathcal{E}_{\rm el}-E_{\rm a})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q|\phi_{\rm el}\,\chi\rangle \\ & +\langle\phi_{\rm el}\,\chi|Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(H_{\rm n}+\mathcal{E}_{\rm el}-E_{\rm a})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}|\phi_{\rm el}\,\chi\rangle \\ & +\langle\phi_{\rm el}\,\chi|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(Q-\langle Q\rangle^{(0)})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}|\phi_{\rm el}\,\chi\rangle. \end{aligned}\tag{37}$$

Additional corrections due to $\delta\chi$ in Eq.(24) can easily be included in the $\langle Q\rangle^{(0)}$ and $\langle Q\rangle^{(1)}$ by replacing χ by $\chi+\delta\chi$ and will not be considered any further. Let us return now to the leading order correction to the matrix element in Eq. (36)

$$\langle Q\rangle^{(1)} = \int d^3R\,\Big\{(\chi^*_{\rm f}\,\chi_{\rm i})\,\Big[\langle H_{\rm n}\,\phi_{\rm el}|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q\,|\phi_{\rm el}\rangle + \langle\phi_{\rm el}|Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,|H_{\rm n}\,\phi_{\rm el}\rangle\Big]$$

$$
\begin{aligned}
&- \frac{\vec{\nabla}(\chi_{\rm f}^*\,\chi_{\rm i})}{2\,m_{\rm n}}\Big[\langle\vec{\nabla}_R\phi_{\rm el}|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q\,|\phi_{\rm el}\rangle+\langle\phi_{\rm el}|Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,|\vec{\nabla}_R\phi_{\rm el}\rangle\Big] \\
&- \frac{\Big(\chi_{\rm i}\,\vec{\nabla}\chi_{\rm f}^*-\chi_{\rm f}^*\,\vec{\nabla}\chi_{\rm i}\Big)}{2\,m_{\rm n}}\Big[\langle\vec{\nabla}_R\phi_{\rm el}|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q\,|\phi_{\rm el}\rangle-\langle\phi_{\rm el}|Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,|\vec{\nabla}_R\phi_{\rm el}\rangle\Big]\Big\}
\end{aligned} \tag{38}
$$

and consider two special cases. If Q is a real operator, then the third term vanishes and with the help of integration by parts we obtain

$$
\langle Q\rangle^{(1)} = \langle\chi_{\rm f}|\langle Q\rangle^{(1)}_{\rm el}|\chi_{\rm i}\rangle, \tag{39}
$$

$$
\langle Q\rangle^{(1)}_{\rm el} = \langle\phi_{\rm el}|\,\overset{\leftrightarrow}{H}_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q\,|\phi_{\rm el}\rangle+\langle\phi_{\rm el}|\,Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle, \tag{40}
$$

where for arbitrary $\psi_{\rm el}$ and $\psi'_{\rm el}$:

$$
\langle\psi'_{\rm el}|\overset{\leftrightarrow}{H}_{\rm n}|\psi_{\rm el}\rangle = \langle\vec{\nabla}_R\,\psi'_{\rm el}|\vec{\nabla}_R\,\psi_{\rm el}\rangle/(2\,m_{\rm n})+\langle\psi'_{\rm el}|H''_{\rm n}|\psi_{\rm el}\rangle. \tag{41}
$$

This case of the real Hermitian Q finds applications in studying relativistic corrections to rovibrational energies and to all electric properties. If $Q=\vec{Q}$ is an imaginary vector operator composed of electronic operators and $\vec{R}$, such that $\vec{R}\cdot\vec{Q}=0$, then the first two terms in Eq. (38) vanish and

$$
\begin{aligned}
\langle Q^i\rangle^{(1)} &= \frac{1}{2\,m_{\rm n}}\int\frac{d^3R}{R^2}\,[(J^i_{\rm n}\,\chi_{\rm f})^*\,\chi_{\rm i}+\chi_{\rm f}^*\,(J^i_{\rm n}\,\chi_{\rm i})] \\
&\quad\times\Big[\langle\phi_{\rm el}|Q^j\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}|J^j_{\rm n}\phi_{\rm el}\rangle+\langle J^j_{\rm n}\phi_{\rm el}|\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q^j|\phi_{\rm el}\rangle\Big],
\end{aligned} \tag{42}
$$

where $\vec{J}_{\rm n}$ is defined in Eq. (17). Let us assume that $\phi_{\rm el}$ is a Σ state, so that $\vec{J}_{\rm n}\,|\phi_{\rm el}\rangle = -\vec{J}_{\rm el}\,|\phi_{\rm el}\rangle$ and

$$
\langle Q^i\rangle^{(1)} = -\Big\langle\chi_{\rm f}\Big|\,\frac{J^i_{\rm n}}{m_{\rm n}\,R^2}\,\langle\phi_{\rm el}|J^j_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q^j|\phi_{\rm el}\rangle\,\Big|\chi_{\rm i}\Big\rangle. \tag{43}
$$

This case of imaginary Hermitian Q finds application in studying magnetic properties of molecules.

B. Second order matrix elements

Consider the second order matrix element with two arbitrary electronic operators Q_1 and Q_2. Let us assume that $\langle\phi_{\rm el}|Q_i|\phi_{\rm el}\rangle=0$ and introduce the notation

$$
\langle Q_1\,Q_2\rangle \equiv \langle\phi|Q_1\,\frac{1}{(E-H)'}\,Q_2|\phi\rangle+\text{c.c.} \tag{44}
$$

In the leading order of NAPT this matrix element is

$$\langle Q_1\, Q_2\rangle^{(0)} = \langle\chi|\langle Q_1\, Q_2\rangle^{(0)}_{\rm el}|\chi\rangle, \tag{45}$$

$$\langle Q_1\, Q_2\rangle^{(0)}_{\rm el} = \langle\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\rangle + {\rm c.c.}, \tag{46}$$

and the nonadiabatic correction is

$$\begin{aligned}\langle Q_1\, Q_2\rangle^{(1)} = {}& \langle\chi\,\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(H_{\rm n}+\mathcal{E}_{\rm el}-E_{\rm a})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\,\chi\rangle\\ &+\langle\chi\,\phi_{\rm el}|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_1\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\,\chi\rangle\\ &+\langle\chi\,\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}|\phi_{\rm el}\,\chi\rangle + {\rm c.c.}\,.\end{aligned} \tag{47}$$

This correction can also be rewritten in terms of the nested electronic matrix element, namely

$$\langle Q_1\, Q_2\rangle^{(1)} = \langle\chi|\langle Q_1\, Q_2\rangle^{(1)}_{\rm el}|\chi\rangle \tag{48}$$

$$\begin{aligned}\langle Q_1\, Q_2\rangle^{(1)}_{\rm el} = {}& \langle\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(\overleftrightarrow{H}_{\rm n}-\mathcal{E}_{\rm a})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\rangle\\ &+\langle\phi_{\rm el}|\,\overleftrightarrow{H}_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_1\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\rangle\\ &+\langle\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\overleftrightarrow{H}_{\rm n}\,|\phi_{\rm el}\rangle + {\rm c.c.}\,.\end{aligned} \tag{49}$$

These formulae will be used in the calculations of the nonadiabatic corrections to the shielding constant. The more general case with $\langle\phi_{\rm el}|Q_i|\phi_{\rm el}\rangle \neq 0$ for Hermitian real operators Q_i is considered in the following section using a slightly different approach.

C. Diagonal matrix elements with real Hermitian operators

The finite nuclear mass corrections to the diagonal matrix element of a Hermitian and real operator Q can obtained by taking a derivative δ_Q with respect to Q of the nuclear Schrödinger equation, which includes the diagonal adiabatic correction $\mathcal{E}_{\rm a}$ in Eq. (21)

$$\delta_Q[H_{\rm n}+\mathcal{E}_{\rm a}(R)+\mathcal{E}_{\rm el}(R)-E_{\rm a}]\,|\chi\rangle = 0\,, \tag{50}$$

that is

$$[H_{\rm n}+\mathcal{E}_{\rm a}(R)+\mathcal{E}_{\rm el}(R)-E_{\rm a}]\,|\delta_Q\chi\rangle + [\delta_Q\mathcal{E}_{\rm a}(R)+\delta_Q\mathcal{E}_{\rm el}(R)-\delta_Q E_{\rm a}]\,|\chi\rangle = 0\,. \tag{51}$$

Taking the product with $\langle\chi|$ on the left hand side, one obtains the matrix element with the leading finite nuclear mass corrections

$$\langle\phi|Q|\phi\rangle = \delta_Q E \approx \delta_Q E_{\rm a} = \langle\chi|\delta_Q\mathcal{E}_{\rm el}(R) + \delta_Q\mathcal{E}_{\rm a}(R)|\chi\rangle. \tag{52}$$

The perturbation of electronic energies $\mathcal{E}_{\rm el}(R)$ and $\mathcal{E}_{\rm a}(R)$ due to some operator Q can be obtained using standard Rayleigh-Schrödinger perturbation theory and the result

$$\langle\phi|Q|\phi\rangle = \langle\chi|\langle Q\rangle^{(0)}_{\rm el}|\chi\rangle + \langle\chi|\langle Q\rangle^{(1)}_{\rm el}|\chi\rangle + \ldots \tag{53}$$

coincides with the former derivation. The fact that leading finite nuclear mass corrections to the matrix elements can be obtained from the adiabatic nuclear equation simplifies their derivation.

For the corrections to the second order matrix element we will need $\delta_Q|\chi\rangle$, which is

$$\begin{aligned}\delta_Q|\chi\rangle \;=\; & \frac{1}{[E_{\rm a} - H_{\rm n} - \mathcal{E}_{\rm a}(R) - \mathcal{E}_{\rm el}(R)]'}\Big[\langle\phi_{\rm el}|Q|\phi_{\rm el}\rangle \\ & +\langle\phi_{\rm el}|H_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q|\phi_{\rm el}\rangle + \langle\phi_{\rm el}|Q\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,H_{\rm n}|\phi_{\rm el}\rangle\Big]\,|\chi\rangle.\end{aligned} \tag{54}$$

Consider now the second order matrix element $\langle Q_1\ Q_2\rangle$ in Eq. (44) with two electronic operators Q_1 and Q_2. In order to find the Born-Oppenheimer form and the finite nuclear mass corrections, we take the second order derivative $\delta_{Q_1Q_2}$ of Eq. (21), and multiply from the left by $\langle\chi|$

$$\begin{aligned}&\langle\chi|\delta_{Q_1Q_2}\mathcal{E}_{\rm a}(R) + \delta_{Q_1Q_2}\mathcal{E}_{\rm el}(R) - \delta_{Q_1Q_2}E_{\rm a}\,|\chi\rangle + \langle\chi|\delta_{Q_1}\mathcal{E}_{\rm a}(R) + \delta_{Q_1}\mathcal{E}_{\rm el}(R)\,|\delta_{Q_2}\chi\rangle \\ &+\langle\chi|\delta_{Q_2}\mathcal{E}_{\rm a}(R) + \delta_{Q_2}\mathcal{E}_{\rm el}(R)\,|\delta_{Q_1}\chi\rangle = 0\,.\end{aligned} \tag{55}$$

This second order matrix element $\langle Q_1\ Q_2\rangle$ is identified with $\delta_{Q_1Q_2}E_{\rm a}$, and thus

$$\begin{aligned}\langle Q_1\ Q_2\rangle \;=\; & \langle\phi|Q_1\,\frac{1}{(E-H)'}\,Q_2|\phi\rangle + \langle\phi|Q_2\,\frac{1}{(E-H)'}\,Q_1|\phi\rangle \\ =\; & \langle\chi|\delta_{Q_1Q_2}\mathcal{E}_{\rm el}(R)\,|\chi\rangle + \langle\chi|\delta_{Q_1}\mathcal{E}_{\rm el}(R)\,|\delta_{Q_2}\chi\rangle + \langle\chi|\delta_{Q_2}\mathcal{E}_{\rm el}(R)\,|\delta_{Q_1}\chi\rangle \\ & +\langle\chi|\delta_{Q_1Q_2}\mathcal{E}_{\rm a}(R)|\chi\rangle + \langle\chi|\delta_{Q_1}\mathcal{E}_{\rm a}(R)|\delta_{Q_2}\chi\rangle + \langle\chi|\delta_{Q_2}\mathcal{E}_{\rm a}(R)|\delta_{Q_1}\chi\rangle + \ldots \\ =\; & \langle Q_1\,Q_2\rangle^{(0)} + \langle Q_1\,Q_2\rangle^{(1)} + \ldots,\end{aligned} \tag{56}$$

where $\delta_{Q_1Q_2}\mathcal{E}_{\rm el}$ and $\delta_{Q_1Q_2}\mathcal{E}_{\rm a}$ are corrections to corresponding energies due to electronic operators Q_1 and Q_2, and

$$\begin{aligned}\langle Q_1\,Q_2\rangle^{(0)} \;=\; & \langle\chi|\langle\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\rangle|\chi\rangle + \\ & +\langle\chi|\,\langle Q_1\rangle^{(0)}_{\rm el}\,\frac{1}{[E_{\rm a} - H_{\rm n} - \mathcal{E}_{\rm a}(R) - \mathcal{E}_{\rm el}(R)]'}\,\langle Q_2\rangle^{(0)}_{\rm el}\,|\chi\rangle + \text{c.c.}\,,\end{aligned} \tag{57}$$

and

$$\begin{aligned}
\langle Q_1\, Q_2\rangle^{(1)} &= \langle\chi|\,\langle\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(\overset{\leftrightarrow}{H}_{\rm n}-\mathcal{E}_{\rm a})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\rangle\,|\chi\rangle \\
&+\langle\chi|\,\langle\phi_{\rm el}|\,\overset{\leftrightarrow}{H}_{\rm n}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(Q_1-\langle Q_1\rangle^{(0)}_{\rm el})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,Q_2|\phi_{\rm el}\rangle\,|\chi\rangle \\
&+\langle\chi|\,\langle\phi_{\rm el}|Q_1\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(Q_2-\langle Q_2\rangle^{(0)}_{\rm el})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle\,|\chi\rangle \\
&+\langle\chi|\,\langle Q_1\rangle^{(1)}_{\rm el}\,\frac{1}{[E_{\rm a}-H_{\rm n}-\mathcal{E}_{\rm a}(R)-\mathcal{E}_{\rm el}(R)]'}\,\langle Q_2\rangle^{(0)}_{\rm el}\,|\chi\rangle \\
&+\langle\chi|\,\langle Q_1\rangle^{(0)}_{\rm el}\,\frac{1}{[E_{\rm a}-H_{\rm n}-\mathcal{E}_{\rm a}(R)-\mathcal{E}_{\rm el}(R)]'}\,\langle Q_2\rangle^{(1)}_{\rm el}\,|\chi\rangle + \text{c.c.}\,. \qquad (58)
\end{aligned}$$

In the case $\langle Q_1\rangle^{(0)}_{\rm el} = \langle Q_2\rangle^{(0)}_{\rm el} = 0$ the above formulae coincide with those derived in the previous subsection.

D. Matrix elements of Hermitian operators with R-derivatives

Consider an operator of the form $Q = \vec{Q}\cdot\vec{P}$ where $\vec{P} = -i\,\vec{\nabla}_R$, and $\vec{Q}$ is a Hermitian, electronic operator, such that $[P^i\,,\,Q^i] = 0$, for example the electron-nucleus Breit interaction Eq. (65). Its matrix element between different rovibrational states is of the form

$$\begin{aligned}
\langle\phi_{\rm el}\,\chi_{\rm f}|Q|\phi_{\rm el}\,\chi_{\rm i}\rangle &= \frac{i}{2}\,\langle\chi_{\rm f}|\Big[\langle\vec{\nabla}_R\,\phi_{\rm el}|\vec{Q}|\phi_{\rm el}\rangle - \langle\phi_{\rm el}|\vec{Q}|\vec{\nabla}_R\phi_{\rm el}\rangle\Big]|\chi_{\rm i}\rangle \\
&+\frac{i}{2}\Big[\langle\vec{\nabla}\chi_{\rm f}|\langle\vec{Q}\rangle_{\rm el}|\chi_{\rm i}\rangle - \langle\chi_{\rm f}|\langle\vec{Q}\rangle_{\rm el}|\vec{\nabla}\chi_{\rm i}\rangle\Big]. \qquad (59)
\end{aligned}$$

If $\vec{Q}$ is an imaginary operator, then the second term vanishes and

$$\begin{aligned}
\langle\phi_{\rm el}\,\chi_{\rm f}|Q|\phi_{\rm el}\,\chi_{\rm i}\rangle &= \langle\chi_{\rm f}|\langle Q\rangle_{\rm el}|\chi_{\rm i}\rangle, \qquad (60)\\
\langle Q\rangle_{\rm el} &= -i\,\langle\phi_{\rm el}|\vec{Q}|\vec{\nabla}_R\,\phi_{\rm el}\rangle = i\,\langle\vec{\nabla}_R\,\phi_{\rm el}|\vec{Q}|\phi_{\rm el}\rangle. \qquad (61)
\end{aligned}$$

If $\vec{Q}$ is a real operator, then the first term in Eq. (59) vanishes and

$$\langle\phi_{\rm el}\,\chi_{\rm f}|Q|\phi_{\rm el}\,\chi_{\rm i}\rangle = \langle\chi_{\rm f}|\langle\vec{Q}\rangle_{\rm el}\cdot\vec{P}|\chi_{\rm i}\rangle = \langle\chi_{\rm f}|\,\overset{\leftarrow}{P}\cdot\langle\vec{Q}\rangle_{\rm el}|\chi_{\rm i}\rangle. \qquad (62)$$

IV. RELATIVISTIC RECOIL CORRECTION TO ROVIBRATIONAL ENERGIES

This is the first and the simplest application of NAPT, the finite nuclear mass correction to the relativistic energy. The total relativistic correction to the binding energy of a Σ state, neglecting interactions with nuclear spins and the higher order $O(m/M)^2$ terms, is given by [8, 9]

$$
\begin{aligned}
\delta H &= \delta H_{\rm el} + \delta H_{\rm n}, &(63)\\
\delta H_{\rm el} &= \alpha^2 \Big[-\sum_a \frac{p_a^4}{8\,m^3} + \sum_{a,X} \frac{Z_X\,\pi}{2\,m^2}\,\delta^3(r_{aX}) + \sum_{a>b} \frac{\pi}{m^2}\,\delta^3(r_{ab}) - \sum_{a>b} \frac{1}{2\,m^2}\,p_a^i \left(\frac{\delta^{ij}}{r_{ab}} + \frac{r_{ab}^i\,r_{ab}^j}{r_{ab}^3}\right) p_b^j\Big] &(64)\\
\delta H_{\rm n} &= \alpha^2 \sum_{a,X} \frac{Z_X}{2\,m\,m_X}\,p_a^i \left(\frac{\delta^{ij}}{r_{aX}} + \frac{r_{aX}^i\,r_{aX}^j}{r_{aX}^3}\right) p_X^j. &(65)
\end{aligned}
$$

The relativistic correction $E_{\rm rel}$ to the energy, taking into account the transformation in Eq. (9), is

$$
\begin{aligned}
E_{\rm rel} &= \langle\phi|\delta H|\phi\rangle &(66)\\
&= \langle\chi|\langle\delta H\rangle^{(0)}_{\rm el}|\chi\rangle + \langle\chi|\langle\delta H\rangle^{(1)}_{\rm el}|\chi\rangle + O(m/M)^{3/2}, &(67)
\end{aligned}
$$

where

$$
\begin{aligned}
\langle\delta H\rangle^{(0)}_{\rm el} &= \langle\phi_{\rm el}|\delta H_{\rm el}|\phi_{\rm el}\rangle \equiv \langle\delta H_{\rm el}\rangle_{\rm el}, &(68)\\
\langle\delta H\rangle^{(1)}_{\rm el} &= \langle\phi_{\rm el}|\delta H_{\rm n}|\phi_{\rm el}\rangle - m\left(\frac{\varepsilon_A}{m_A} - \frac{\varepsilon_B}{m_B}\right)\langle\phi_{\rm el}|[\sum_a \vec{x}_a\cdot\vec{\nabla}_R\,,\,\delta H_{\rm el}]|\phi_{\rm el}\rangle\\
&\quad +2\,\langle\phi_{\rm el}|\delta H_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle. &(69)
\end{aligned}
$$

As has already been noted in [5], relativistic recoil effects are of order $O(m/M)$ and can be expressed as a correction $\langle\delta H\rangle^{(1)}_{\rm el}$ to the BO energy $\mathcal{E}_{\rm el}(R)$.

Since the wave function ϕ does not depend on $\vec{R}_G$, the momentum $\vec{P}_G$ implicitly present in $\delta H_{\rm n}$ can be set to 0. Moreover, we chose $\vec{R}_G$ in dependence on the particular operator in $\delta H_{\rm el}$, in such a way that the result of the transformation ϕ in Eq. (9), namely the second term in Eq. (69), vanishes. For example, for the first, third and fourth term in $\delta H_{\rm el}$ $\vec{R}_G$ is the nuclear mass center ($\varepsilon_A = m_A/(m_A+m_B), \varepsilon_B = m_B/(m_A+m_B)$), for $\delta^3(r_{aX})$ $\vec{R}_G$ is placed at the nucleus X ($\varepsilon_X = 1$), and for $\delta H_{\rm n}$ in the geometrical center ($\varepsilon_A = \varepsilon_B = 1/2$). In this particular choice of $\vec{R}_G$, the derivative $\partial\delta H_{\rm el}/\partial R$ that comes from $H'_{\rm n}$ in Eq. (69) also vanishes and the relativistic finite nuclear mass correction can be rewritten in the form

$$
\begin{aligned}
\langle\delta H\rangle^{(1)}_{\rm el} &= \langle\phi_{\rm el}|\delta H_{\rm n}|\phi_{\rm el}\rangle + 2\,\langle\phi_{\rm el}|\delta H_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\left(H''_{\rm n} + \frac{\vec{J}^2_{\rm el}}{2\,m_{\rm n}\,R^2}\right)|\phi_{\rm el}\rangle\\
&\quad +\frac{1}{m_{\rm n}}\,\langle\phi_{\rm el}|\frac{\partial V}{\partial R}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,(\delta H_{\rm el} - \langle\delta H_{\rm el}\rangle_{\rm el})\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'^2}\,\frac{\partial V}{\partial R}|\phi_{\rm el}\rangle\\
&\quad +\frac{1}{m_{\rm n}}\,\langle\phi_{\rm el}|\delta H_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\frac{\partial(V-\mathcal{E}_{\rm el})}{\partial R}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'^2}\,\frac{\partial V}{\partial R}|\phi_{\rm el}\rangle. &(70)
\end{aligned}
$$

The expectation value of $\delta H_{\rm n}$ is calculated according to Eq. (32), namely if

$$\delta H_{\rm n} = \vec{Q}_1 \cdot \vec{\nabla}_R + Q_2, \tag{71}$$

with Q_i electronic operators and $\vec{\nabla}_R \, \vec{Q}_1 = 0$, then

$$\langle\phi_{\rm el}|\delta H_{\rm n}|\phi_{\rm el}\rangle = \langle\phi_{\rm el}|Q_2|\phi_{\rm el}\rangle + \langle\phi_{\rm el}|\vec{n}\cdot\vec{Q}_1\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\frac{\partial V}{\partial R}|\phi_{\rm el}\rangle + \frac{i}{R}\,\langle\phi_{\rm el}|\vec{n}\times\vec{Q}_1\cdot\vec{J}_{\rm n}|\phi_{\rm el}\rangle. \tag{72}$$

One may expect significant cancellations in the leading finite nuclear mass correction $\langle\delta H\rangle^{(1)}_{\rm el}$ between the first and second terms in Eq. (69). For example, for separate hydrogen atoms in the ground state, this correction vanishes. Therefore, the next order correction, which is $O(m/M)^{3/2}$, may become relatively significant. This is due to, for example, the second order in $H_{\rm n}$ nonadiabatic correction given by Eq. (37), or by the orbit-orbit interaction between nuclei.

V. ELECTRIC PROPERTIES

We will study here the nonadiabatic corrections to the transition dipole moment and the electric dipole static polarizability. The direct nonadiabatic calculations have only been performed for simple molecules like H_2^+ in [10–13], H_2 in [1], and LiH in [2]. There is a considerable literature on electric properties of molecules in what we are calling here the adiabatic approximation. Let us mention the extensive review of Bishop [14] and earlier works of Brieger in [15, 16]. We recover here their results for the electric dipole polarizability, and present closed formulae for the nonadiabatic corrections.

The interaction of a neutral molecular system with a homogenous electric field $\vec{E}$ is given by

$$\delta H = -\vec{D}\cdot\vec{E}, \tag{73}$$

where the electric dipole operator $\vec{D}$ is

$$\vec{D} = e\sum_a \vec{x}_a + e_A\,\vec{x}_A + e_B\,\vec{x}_B, \tag{74}$$

and where $\vec{x}_A = \epsilon_B\,\vec{R}$ and $\vec{x}_B = -\epsilon_A\,\vec{R}$. We note that for charged molecular systems, the electric dipole moment has to be defined with respect to the center of mass of the total molecule.

Let us fix the reference frame to the center of the nuclear charge $\epsilon_A = e_A/(e_A + e_B)$, $\epsilon_B = e_B/(e_A+e_B)$, then $\vec{D} = e\,\sum_a \vec{x}_a$ and this $\vec{D}$ is not affected by the unitary transformation in Eq. (9). We will show below that the interaction of the molecule with the homogenous electric field, in spite of including leading finite nuclear mass effects, can be effectively described by the Hamiltonian $H_{\rm eff}$ in the nuclear space

$$H_{\rm eff} = -\vec{D}_{\rm el}(\vec{R})\cdot\vec{E} - \frac{\alpha^{ij}_{\rm el}(\vec{R})}{2}\,E^i\,E^j\,, \tag{75}$$

where $\vec{D}_{\rm el}(\vec{R})$ is given in Eq. (78) and $\alpha^{ij}_{\rm el}(\vec{R})$ in Eq. (82). From the above equation, the transition dipole moment is

$$\vec{D}_{\rm fi} = \langle\chi_{\rm f}|\vec{D}_{\rm el}|\chi_{\rm i}\rangle, \tag{76}$$

and one notes that the matrix elements $\vec{D}_{\rm fi}$ between the same nuclear states always vanish. Similarly, the total electric dipole static polarizability is

$$\alpha^{ij} = \langle\chi|\alpha^{ij}_{\rm el}|\chi\rangle - 2\,\langle\chi|D^i_{\rm el}\,\frac{1}{E_{\rm a} - H_{\rm n} - \mathcal{E}_{\rm a} - \mathcal{E}_{\rm el}}\,D^j_{\rm el}|\chi\rangle, \tag{77}$$

where the first term is due to the electron excitations and the second one is due to the rovibrational excitations. For molecules with the so called permanent electric dipole moment the second term dominates, with particularly significant contributions coming from intermediate nuclear states with the same vibrational number, but different J.

The electronic matrix elements $\vec{D}_{\rm el}$ and $\alpha_{\rm el}$ are obtained as follows. According to Eqs. (35,40) and Eqs. (29,30) the electric dipole moment including the leading nonadiabatic effects is

$$\vec{D}_{\rm el} = \vec{D}^{(0)}_{\rm el} + \vec{D}^{(1)}_{\rm el}, \tag{78}$$

where

$$\vec{D}^{(0)}_{\rm el} = \langle\phi_{\rm el}|\vec{D}|\phi_{\rm el}\rangle, \tag{79}$$

$$\vec{D}^{(1)}_{\rm el} = 2\,\langle\phi_{\rm el}|\vec{D}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\overleftrightarrow{H}_{\rm n}\,|\phi_{\rm el}\rangle. \tag{80}$$

For Σ electronic states the nonadiabatic correction can be rewritten in the form

$$\begin{aligned}\vec{D}^{(1)}_{\rm el} =&\ 2\,\langle\phi_{\rm el}|\vec{D}\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\Big(H''_{\rm n} + \frac{\vec{J}^2_{\rm el}}{2\,m_{\rm n}\,R^2}\Big)|\phi_{\rm el}\rangle + \frac{i}{m_{\rm n}\,R^2}\,\langle\phi_{\rm el}|\vec{D}\times\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\vec{J}_{\rm el}|\phi_{\rm el}\rangle\\ &+\frac{1}{m_{\rm n}}\,\langle\phi_{\rm el}|\vec{D}\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\frac{\partial(V - \mathcal{E}_{\rm el})}{\partial R}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'^2}\,\frac{\partial V}{\partial R}\,|\phi_{\rm el}\rangle\\ &+\frac{1}{m_{\rm n}}\,\langle\phi_{\rm el}|\frac{\partial V}{\partial R}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,(\vec{D} - \vec{D}^{(0)}_{\rm el})\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'^2}\,\frac{\partial V}{\partial R}\,|\phi_{\rm el}\rangle.\end{aligned} \tag{81}$$

This result is in agreement with the previously obtained much simpler formula for the HD molecule [17], where only the last term in H_n contributes in the above equation due to the inversion symmetry of the ground electronic state. We observe that in spite of including first order nonadiabatic corrections, the transition dipole moment $\vec{D}_\mathrm{fi}$ can be represented in terms of the matrix element of the electronic dipole moment $\vec{D}_\mathrm{el}$ evaluated with nuclear functions χ_f^* and χ_i, see Eq. (39). A similar result holds for the electric dipole static polarizability

$$\alpha_\mathrm{el}^{ij} = \alpha_\mathrm{el}^{(0)\,ij} + \alpha_\mathrm{el}^{(1)\,ij}, \tag{82}$$

which in the BO approximation is

$$\alpha_\mathrm{el}^{(0)\,ij} = -2\,\langle\phi_\mathrm{el}|D^i\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}\,D^j|\phi_\mathrm{el}\rangle, \tag{83}$$

and the nonadiabatic correction, using Eq. (58) is

$$\begin{aligned}\alpha_\mathrm{el}^{(1)\,ij} \;=\; -2\Big[&\langle\phi_\mathrm{el}|D^i\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}(\overleftrightarrow{H}_\mathrm{n}-\mathcal{E}_\mathrm{a})\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}\,D^j|\phi_\mathrm{el}\rangle\\ &+\langle\phi_\mathrm{el}|\,\overleftrightarrow{H}_\mathrm{n}\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}(D^i-D_\mathrm{el}^{(0)\,i})\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}\,D^j|\phi_\mathrm{el}\rangle\\ &+\langle\phi_\mathrm{el}|D^i\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}(D^j-D_\mathrm{el}^{(0)\,j})\,\frac{1}{(\mathcal{E}_\mathrm{el}-H_\mathrm{el})'}\,\overleftrightarrow{H}_\mathrm{n}\,|\phi_\mathrm{el}\rangle\Big].\end{aligned} \tag{84}$$

The explicit formula after taking the derivative with respect to R is too lengthy to be written here, but can easily be obtained with the help of Eqs. (29,30,31). Eq. (77) in the adiabatic approximation, namely $\alpha_\mathrm{el}\to\alpha_\mathrm{el}^{(0)}$, $\vec{D}_\mathrm{el}\to\vec{D}_\mathrm{el}^{(0)}$ was already obtained in the literature [14–16]. Results for nonadiabatic corrections when $\alpha_\mathrm{el}\to\alpha_\mathrm{el}^{(1)}$, $\vec{D}_\mathrm{el}\to\vec{D}_\mathrm{el}^{(1)}$ are, in our opinion, new, and have not been discussed in the literature.

VI. MAGNETIC PROPERTIES

We consider here nonadiabatic corrections to magnetic properties of a diatomic molecule. These properties within the BO approximation have been reviewed in detail by Flygare in [18]. Here, we demonstrate that the nonadiabatic corrections can be implemented in the effective nuclear Hamiltonian, similarly to that in the BO approximation, namely

$$H_\mathrm{eff} = -\eta(R)\,\vec{I}\cdot\vec{J} - \gamma_I\,\vec{I}(1-\hat{\sigma}_\mathrm{el}(\vec{R}))\vec{B} - \gamma_J(R)\,\vec{J}\cdot\vec{B} - \frac{1}{2}\,\vec{B}\hat{\chi}(\vec{R})\vec{B}, \tag{85}$$

where it is understood that the electronic part of the angular momentum operator $\vec{J}_\mathrm{el}$ Eq. (17) vanishes on χ, η is the spin-rotation constant, $\mu_I = I\,\gamma_I$ is the nuclear magnetic moment,

$\mu_J = J\,\gamma_j$ is the orbital magnetic moment, $\sigma_{\rm el}$ is the R-dependent shielding constant, $\hat{\chi}$ is the magnetic susceptibility, and $\vec{B}$ is the magnetic field. The Hamiltonian in Eq. (85) should in principle involve also quadrupolar interaction $(I^i\,I^j)^{(2)}\,(J^i\,J^j)^{(2)}$ or $(I^i\,I^j)^{(2)}\,J^i\,B^j$. The first term comes from the quadrupole moment of nucleus or tensor interactions between nuclear magnetic moments, while the second term has not been investigated in the literature so far. Neither term will be considered in this work. If two different nuclei are involved, each one has its own spin and magnetic moment, and the interaction between them should be included, but we do not consider it either. In the following we rederive in a simple way known results for the rotational magnetic moment $\mu_{\rm J}$ and the spin rotation constant η, and obtain nonadiabatic corrections to the shielding constant. These corrections, to our knowledge, have not yet been investigated in the literature [19].

A. Nonrelativistic Hamiltonian in the external magnetic field

In order to obtain finite nuclear mass corrections we start with the Hamiltonian of a molecular system in a homogenous magnetic field

$$H_0 = \sum_\beta \frac{\vec{\pi}_\beta^2}{2\,m_\beta} + V, \tag{86}$$

where β sums over both electrons and nuclei. We assume the coordinate system as defined in Eqs. (2-4): $\vec{x}_\beta = \vec{r}_\beta - \vec{R}_G$ and perform the following unitary transformation

$$\tilde{H}_0 = e^{-i\,\varphi}\,H_0\,e^{i\,\varphi} + \partial_t\varphi, \tag{87}$$

$$\begin{aligned}\varphi &= \sum_\beta e_\beta \int_0^1 du\,\vec{x}_\beta\cdot\vec{A}(\vec{R}_G + u\,\vec{x}_\beta)\\ &= \sum_\beta e_\beta[x^i_\beta\,A^i + x^i_\beta\,x^j_\beta\,A^i_{,j}/2],\end{aligned} \tag{88}$$

$$\begin{aligned}\pi^j_\beta &= p^j_\beta - e_\beta\,A^j(\vec{r}_\beta)\\ &= p^j_\beta - e_\beta\,[A^j + x^i_\beta\,A^j_{,i}],\end{aligned} \tag{89}$$

where $\vec{A} \equiv \vec{A}(\vec{R}_G)$. The result of this transformation on the canonical momentum is

$$e^{-i\,\varphi}\,\pi^i_a\,e^{i\,\varphi} = p^i_a + \frac{e_a}{2}\,(\vec{x}_a\times\vec{B})^j, \tag{90}$$

$$e^{-i\,\varphi}\,\pi^i_A\,e^{i\,\varphi} = p^i_A + \frac{e_A}{2}\,(\vec{x}_A\times\vec{B})^j + \frac{\epsilon_A}{2}\,(\vec{D}\times\vec{B})^j, \tag{91}$$

$$e^{-i\,\varphi}\,\pi^i_B\,e^{i\,\varphi} = p^i_B + \frac{e_B}{2}\,(\vec{x}_B\times\vec{B})^j + \frac{\epsilon_B}{2}\,(\vec{D}\times\vec{B})^j, \tag{92}$$

where $\vec{D}$ is the total electric dipole moment $\vec{D} = \sum_\beta e_\beta \, \vec{x}_\beta$ and we have assumed that $\sum_\beta e_\beta = 0$, so the molecule is neutral. In consequence, the transformed Hamiltonian does not depend on $\vec{R}_G$, so we are allowed to set $\vec{P}_G = 0$. In order to further simplify, we perform the next transformation as defined in Eq. (9), neglect $O(m/M)^2$ terms, and the transformed Hamiltonian then takes the form

$$
\begin{aligned}
H_0 &= H_{\rm el} + H_{\rm n} + H_\mu + H_\chi, & (93)\\
H_\mu &= -\sum_a \frac{e}{2\,m}\,\vec{x}_a \times \vec{q}_a \cdot \vec{B} + \delta H_\mu, & (94)\\
\delta H_\mu &= -\Big(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\Big)\,\vec{D} \times \vec{P} \cdot \vec{B} - \frac{1}{2}\Big(\frac{1}{m_A} + \frac{1}{m_B}\Big)\,(e_A\,\epsilon_B^2 + e_B\,\epsilon_A^2)\,\vec{R} \times \vec{P} \cdot \vec{B} & \\
&\quad + \frac{1}{2}\Big(\frac{\epsilon_A^2}{m_A} + \frac{\epsilon_B^2}{m_B}\Big)\,\vec{D} \times \sum_a \vec{q}_a \cdot \vec{B} + \frac{\epsilon_A\,\epsilon_B}{2}\Big(\frac{e_A}{m_A} - \frac{e_B}{m_B}\Big)\,\vec{R} \times \sum_a \vec{q}_a \cdot \vec{B}, & (95)\\
H_\chi &= \sum_a \frac{e^2}{8\,m}\,(\vec{x}_a \times \vec{B})^2 + \delta H_\chi, & (96)\\
\delta H_\chi &= \frac{1}{8\,m_A}\,(e_A\,\vec{x}_A \times \vec{B} + \epsilon_A\,\vec{D} \times \vec{B})^2 + \frac{1}{8\,m_B}\,(e_B\,\vec{x}_B \times \vec{B} + \epsilon_B\,\vec{D} \times \vec{B})^2. & (97)
\end{aligned}
$$

The center of the reference frame $\vec{R}_G$ is placed arbitrarily on the symmetry axis. This freedom will be used below to simplify formulae for nonadiabatic corrections.

B. Rotational magnetic moment

The rotational magnetic moment was first investigated by Wick in [20] for H_2, and later by Ramsey, who extended Wick's result to arbitrary masses of nuclei, and performed first measurements in Ref. [21], later presenting improved measurements with Harrick in Ref. [22]. The rotational magnetic moments results from coupling of the molecular rotation to the magnetic field. The expectation value on the Σ state of the first term in Eq. (94) $e/(2\,m)\,\vec{J}_{\rm el} \cdot \vec{B}$ vanishes, so that the leading coupling comes from nonadiabatic corrections to the matrix element as given by Eq. (43) and from δH_μ, namely

$$
\gamma_J = \Big(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\Big)\,\frac{\vec{D}_{\rm el} \cdot \vec{R}}{R^2} + \frac{(e_A\,\epsilon_B^2 + e_B\,\epsilon_A^2)}{2\,m_{\rm n}} - \frac{e}{2\,m}\,\frac{1}{m_{\rm n}\,R^2}\,\langle\phi_{\rm el}|\vec{J}_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\vec{J}_{\rm el}|\phi_{\rm el}\rangle. \qquad (98)
$$

In the center of nuclear mass frame $\epsilon_A = m_A/(m_A + m_B)$, $\epsilon_B = m_B/(m_A + m_B)$ the rotational magnetic moment in units of the nuclear magneton μ_I becomes

$$
\frac{\gamma_J}{\mu_I} = \frac{\mu_{\rm J}}{J\,\mu_I} = m_{\rm n}\,m_p\,\Big(\frac{Z_A}{m_A^2} + \frac{Z_B}{m_B^2}\Big) + \frac{m_p}{m_{\rm n}\,m\,R^2}\,\langle\phi_{\rm el}|J^i_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,J^i_{\rm el}|\phi_{\rm el}\rangle, \qquad (99)
$$

where m_p is the proton mass, in agreement with the result from Ref. [21] [Eq. (4) with assuming $Z_A = Z_B = 1$]. One observes that rotational magnetic moment in Eq. (98) does not depend on the choice of reference frame, but does depend on the distance R between nuclei. For large R it vanishes at least as fast as R^{-6}. The dependence of γ_J on R leads to the appearance of the magnetic dipole transition in H_2, between states of the same angular momentum, but of different vibrational number. These transitions, to our knowledge, have not yet been investigated in the literature, and may play a role in the astrophysical environment: their importance should be verified by explicit calculations.

As was first noted in Ref. [22] the rotational magnetic moment is related to the paramagnetic part of magnetic susceptibility χ. In the BO approximation $\chi_{\rm el}$ is given by

$$\chi^{ij}_{\rm el} = -\frac{e^2}{4\,m}\sum_a \langle\phi_{\rm el}|\vec{x}_a^2\delta^{ij} - x_a^i\,x_a^j|\phi_{\rm el}\rangle - \frac{e^2}{2\,m^2}\,\langle\phi_{\rm el}|J^i_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,J^j_{\rm el}|\phi_{\rm el}\rangle. \tag{100}$$

For Σ states it can be simplified to the form

$$\begin{aligned}\chi^{ij}_{\rm el} \;=\; & -\frac{e^2}{8\,m}\sum_a\Big[2\,\langle\phi_{\rm el}|\vec{x}_a^2 - (\vec{n}\cdot\vec{x}_a)^2|\phi_{\rm el}\rangle\,n^i\,n^j + \langle\phi_{\rm el}|\vec{x}_a^2 + (\vec{n}\cdot\vec{x}_a)^2|\phi_{\rm el}\rangle\,(\delta^{ij} - n^i\,n^j)\\ & -\frac{e^2}{4\,m^2}\,\langle\phi_{\rm el}|\vec{J}_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\vec{J}_{\rm el}|\phi_{\rm el}\rangle\,(\delta^{ij} - n^i\,n^j),\end{aligned} \tag{101}$$

The last terms in both Eqs. (98) and (101), which are the second order matrix elements, are similar, while the first terms in both equations are simple to evaluate. This allows one to express the difficult to measure magnetic susceptibility in terms of the rotational magnetic moment. This relation, however, works only in the BO approximation, as nonadiabatic corrections will be different. As noticed by the Authors of [23], this second order matrix element with $\vec{J}_{\rm el}$ operator is present also in the nonadiabatic equation for the nuclear function χ as the $W_\perp$ function (in the notation from our previous work [3]).

C. Spin-rotation Hamiltonian

The general spin-orbit Hamiltonian for arbitrary nuclei, including the external magnetic field is ($\hbar = c = 1$) [8, 9, 24]

$$\delta H = \sum_{\alpha,\beta}\frac{e_\alpha\,e_\beta}{4\,\pi}\,\frac{1}{2\,r_{\alpha\beta}^3}\,\Big[\frac{g_\alpha}{m_\alpha\,m_\beta}\,\vec{s}_\alpha\cdot\vec{r}_{\alpha\beta}\times\vec{\pi}_\beta - \frac{(g_\alpha-1)}{m_\alpha^2}\,\vec{s}_\alpha\cdot\vec{r}_{\alpha\beta}\times\vec{\pi}_\alpha\Big], \tag{102}$$

where the summation over α, β goes over electrons and nuclei. In particular, the coupling of the nuclear spin $\vec{I} = \vec{s}_A$ to the rotation and to the magnetic field using Eq. (102) is

$$\begin{aligned}
\delta H &= \sum_b \frac{e_A\, e}{4\,\pi}\, \frac{\vec{I}}{2\, r_{Ab}^3}\left[\frac{g_A}{m_A\, m}\, \vec{r}_{Ab} \times \vec{\pi}_b - \frac{(g_A - 1)}{m_A^2}\, \vec{r}_{Ab} \times \vec{\pi}_A\right] \\
&+ \frac{e_A\, e_B}{4\,\pi}\, \frac{\vec{I}}{2\, r_{AB}^3}\left[\frac{g_A}{m_A\, m_B}\, \vec{r}_{AB} \times \vec{\pi}_B - \frac{(g_A - 1)}{m_A^2}\, \vec{r}_{AB} \times \vec{\pi}_A\right].
\end{aligned} \tag{103}$$

For convenience, we chose the reference frame centered at the considered nucleus $\vec{R}_G = \vec{R}_A$, so $\epsilon_A = 1$,$\epsilon_B = 0$, perform unitary transformations in Eqs. (88,9), and obtain

$$\begin{aligned}
\delta H &= -\sum_b \frac{e_A\, e}{4\,\pi}\, \frac{\vec{I}}{2\, m_A} \times \frac{\vec{x}_b}{x_b^3} \cdot \left[\frac{g_A}{m}\Big(\vec{q}_b + \frac{m}{m_A}\vec{P} + \frac{e}{2}\, \vec{x}_b \times \vec{B}\Big) - \frac{(g_A - 1)}{m_A}\Big(\vec{P} - \vec{q}_{\rm el} + \frac{\vec{D}}{2} \times \vec{B}\Big)\right] \\
&- \frac{e_A\, e_B}{4\,\pi}\, \frac{\vec{I}}{2\, m_A} \times \frac{\vec{R}}{R^3} \cdot \left[\frac{g_A}{m_B}\left(\vec{P} + \frac{e_B}{2}\, \vec{R} \times \vec{B}\right) + \frac{(g_A - 1)}{m_A}\left(\vec{P} - \vec{q}_{\rm el} + \frac{\vec{D}}{2} \times \vec{B}\right)\right],
\end{aligned} \tag{104}$$

where $\vec{q}_{\rm el} = \sum_a \vec{q}_a$, $\vec{x}_{\rm el} = \sum_a \vec{x}_a$, and the electric dipole operator is $\vec{D} = e\, \vec{x}_{\rm el} - e_B\, \vec{R}$. This Hamiltonian will be used in next sections to rederive the known formulae for the spin-rotation and the shielding constants, and to obtain a closed expression for the nonadiabatic corrections to the magnetic shielding, which contribute at the level of $m_{\rm e}/m_{\rm n}$ which for H_2 is about 10^{-3}.

D. Spin-rotation constant

The theory of the spin-rotation interaction was introduced by Wick [20], Ramsey [21], and Foley [25], and further developed by Ramsey [26, 27], by Frosch and Foley [28] and again by Ramsey [29]. These theoretical results were not in agreement for a long time, until Reid and Chu in [30] found a complete set of corrections. Here we rederive their result on the basis of Eq. (104).

The spin-rotation interactions results from δH above with $\vec{B} = 0$. For considered Σ states terms with $\vec{q}_{\rm el}$ vanish and δH takes the form

$$\delta H = \vec{Q}_1 \cdot \vec{I} + \vec{Q}_2 \times \vec{P} \cdot \vec{I}, \tag{105}$$

$$\vec{Q}_1 = -\sum_b \frac{e_A\, e}{4\,\pi}\, \frac{g_A}{2\, m\, m_A}\, \frac{\vec{x}_b \times \vec{q}_b}{x_b^3}, \tag{106}$$

$$\vec{Q}_2 = -\sum_b \frac{e_A\, e}{4\,\pi}\, \frac{1}{2\, m_A^2}\, \frac{\vec{x}_b}{x_b^3} - \frac{e_A\, e_B}{4\,\pi}\, \frac{1}{2\, m_A}\left[\frac{g_A}{m_B} + \frac{(g_A - 1)}{m_A}\right]\frac{\vec{R}}{R^3}. \tag{107}$$

The expectation value of $\langle\phi_{\rm el}|\vec{Q}_1|\phi_{\rm el}\rangle$ vanishes, and $\vec{Q}_1$ operator contributes only through nonadiabatic matrix elements Eq. (43), so the total spin-rotation constant is given by

$$-\eta\,\vec{I}\cdot\vec{J} = -\frac{\vec{I}\cdot\vec{J}}{m_{\rm n}\,R^2}\,\langle\phi_{\rm el}|\vec{J}_{\rm el}\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\,\vec{Q}_1|\phi_{\rm el}\rangle + \langle\phi_{\rm el}|\vec{Q}_2|\phi_{\rm el}\rangle\times\vec{P}\cdot\vec{I}. \tag{108}$$

The expectation value of the first term in $\vec{Q}_2$ can be expressed in terms of derivative of BO energy, namely

$$\langle\phi_{\rm el}|\sum_b\frac{e_A\,e}{4\,\pi}\,\frac{\vec{x}_b}{x_b^3}|\phi_{\rm el}\rangle \;=\; \vec{n}\left(\frac{\partial\mathcal{E}_{\rm el}}{\partial R}+\frac{e_A\,e_B}{4\,\pi}\,\frac{1}{R^2}\right), \tag{109}$$

and thus η in atomic units becomes $[e_X=-Z_X\,e, \alpha=e^2/(4\,\pi)]$

$$\begin{aligned}\eta \;=\; \alpha^2\Big[&\frac{1}{R^2}\,\frac{Z_A\,g_A}{2\,m_{\rm n}\,m_A}\,\langle\phi_{\rm el}|\sum_a\vec{x}_a\times\vec{q}_a\,\frac{1}{(\mathcal{E}_{\rm el}-H_{\rm el})'}\sum_b\frac{\vec{x}_b\times\vec{q}_b}{x_b^3}|\phi_{\rm el}\rangle\\ &+\frac{1}{R}\,\frac{1}{2\,m_A^2}\,\frac{\partial\mathcal{E}_{\rm el}}{\partial R}+\frac{1}{R^3}\,\frac{Z_A\,Z_B\,g_A}{2\,m_A\,m_{\rm n}}\Big],\end{aligned} \tag{110}$$

in agreement with Ref. [30], their C is related to our η by $C = 2\,\pi\,\eta$. Since there is cancellation between the first and the third term, η vanishes at least as fast as R^{-6} for large values of R.

E. Magnetic shielding constant

The shielding of the external magnetic field due to atomic electrons was first considered by Ramsey in [26] with the help of the Breit-Pauli Hamiltonian including the external magnetic field. Here we rederive his result, and in addition obtain nonadiabatic corrections to it. A similar calculation for atoms has recently been performed in [9, 31].

The Hamiltonian of a molecule in the magnetic field including the nuclear spin, but neglecting that of electrons, is a sum of H_0 in Eq. (93) and δH in Eq. (103). In the BO approximation $\hat{\sigma}^{(0)}_{\rm el}$ is a sum of diamagnetic and paramagnetic parts. In atomic units, they are correspondingly

$$\begin{aligned}\vec{I}\,\hat{\sigma}^{(0)}_{\rm el}\vec{B} \;=\; \alpha^2\Big[&-\frac{1}{2}\,\langle\phi_{\rm el}|\sum_b\left(\vec{I}\times\frac{\vec{x}_b}{x_b^3}\right)\cdot(\vec{x}_b\times\vec{B})|\phi_{\rm el}\rangle\\ &+\langle\phi_{\rm el}|\sum_a\vec{x}_a\times\vec{q}_a\cdot\vec{B}\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\,\sum_b\frac{\vec{x}_b\times\vec{q}_b}{x_b^3}\cdot\vec{I}|\phi_{\rm el}\rangle\Big].\end{aligned} \tag{111}$$

Nonadiabatic corrections $\hat{\sigma}^{(1)}_{\rm el}$, namely all corrections which are linear in the electron-nuclear mass ratio, come from several sources, and we split them into four parts

$$\hat{\sigma}^{(1)}_{\rm el} = \hat{\sigma}^{(1)}_{\rm n}+\hat{\sigma}^{(1)}_{\rm d}+\hat{\sigma}^{(1)}_{\rm s}+\hat{\sigma}^{(1)}_{\rm l}. \tag{112}$$

$\hat\sigma_{\rm n}^{(1)}$ is the correction due to $H_{\rm n}$ to the matrix elements in Eq. (111), namely using Eq. (49) one obtains

$$
\begin{aligned}
\vec I\,\hat\sigma_{\rm n}^{(1)}\vec B \;=\; \alpha^2\Big[&-\langle\phi_{\rm el}|\sum_b\Big(\vec I\times\frac{\vec x_b}{x_b^3}\Big)\cdot(\vec x_b\times\vec B)\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\;\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle\\
&+\langle\phi_{\rm el}|\sum_a\vec x_a\times\vec q_a\cdot\vec B\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\,(\overset{\leftrightarrow}{H}_{\rm n}-\mathcal{E}_{\rm a})\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}\cdot\vec I|\phi_{\rm el}\rangle\\
&+\langle\phi_{\rm el}|\;\overset{\leftrightarrow}{H}_{\rm n}\;\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_a\vec x_a\times\vec q_a\cdot\vec B\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}\cdot\vec I|\phi_{\rm el}\rangle\\
&+\langle\phi_{\rm el}|\sum_a\vec x_a\times\vec q_a\cdot\vec B\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}\cdot\vec I\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\;\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle\Big].
\end{aligned}
\tag{113}
$$

$\hat\sigma_{\rm d}^{(1)}$ is a correction to the diamagnetic part due to the direct coupling of the nuclear spin to the magnetic field in δH, Eq. (104)

$$
\begin{aligned}
\vec I\,\hat\sigma_{\rm d}^{(1)}\vec B \;=\;& \frac{\alpha^2}{2\,g_A}\,\langle\phi_{\rm el}\Big|\frac{(g_A-1)}{m_A}\sum_b\Big(\vec I\times\frac{\vec x_b}{x_b^3}\Big)\cdot(\vec x_{\rm el}+Z_B\,\vec R)\times\vec B\\
&-\Big(\vec I\times\frac{\vec R}{R^3}\Big)\cdot\Big[\frac{Z_B^2}{m_B}\,\vec R-\frac{Z_B\,(g_A-1)}{m_A}\,(\vec x_{\rm el}+Z_B\,\vec R)\Big]\times\vec B\Big|\phi_{\rm el}\rangle.
\end{aligned}
\tag{114}
$$

$\hat\sigma_{\rm s}^{(1)}$ is a correction to paramagnetic part due to spin-rotation interaction in δH Eq. (104)

$$
\begin{aligned}
\vec I\,\hat\sigma_{\rm s}^{(1)}\vec B \;=\;& \frac{\alpha^2}{g_A}\,\langle\phi_{\rm el}|\sum_a\vec x_a\times\vec q_a\cdot\vec B\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\Big\{\frac{1}{m_A}\sum_b\vec I\cdot\frac{\vec x_b}{x_b^3}\times\Big[\vec P+(g_A-1)\,\vec q_{\rm el}\Big]\\
&-Z_B\,\vec I\cdot\frac{\vec R}{R^3}\times\Big[\frac{g_A}{m_B}\,\vec P+\frac{(g_A-1)}{m_A}\,(\vec P-\vec q_{\rm el})\Big]\Big\}|\phi_{\rm el}\rangle.
\end{aligned}
\tag{115}
$$

The derivative over nuclear coordinates $\vec P$ in the above and below, can act on the right or on the left, since these matrix elements does not depend on this. Finally, $\hat\sigma_{\rm l}^{(1)}$ is a correction to the paramagnetic part due to δH_μ in Eq. (95),

$$
\begin{aligned}
\vec I\,\hat\sigma_{\rm l}^{(1)}\vec B \;=\;& \alpha^2\,\langle\phi_{\rm el}|\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}\cdot\vec I\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\\
&\Big\{\frac{1}{m_A}\,(\vec x_{\rm el}+Z_B\,\vec R)\times(2\,\vec P-\vec q_{\rm el})-\frac{Z_B}{m_{\rm n}}\,\vec R\times\vec P\Big\}\cdot\vec B|\phi_{\rm el}\rangle.
\end{aligned}
\tag{116}
$$

The total magnetic shielding $\hat\sigma$ is obtained by averaging with the nuclear wave function

$$
\sigma^{ij} = \langle\chi|\sigma_{\rm el}^{(0)ij}+\sigma_{\rm el}^{(1)ij}|\chi\rangle,
\tag{117}
$$

and one notes that the orbital magnetic moment with the spin-rotation coupling gives additional contribution to the shielding constant

$$
\delta\sigma^{ij} = \frac{2}{\gamma_I}\,\langle\chi|\eta\,J^i\,\frac{1}{[E_{\rm a}-H_{\rm n}-\mathcal{E}_{\rm a}-\mathcal{E}_{\rm el}]'}\,\gamma_L\,J^j|\chi\rangle,
\tag{118}
$$

which however is negligible.

Let us present in more details the averaged shielding $\sigma = \sigma^{ii}/3$ in the case of H_2 and isotopomers $Z_A = Z_B = 1$,

$$\sigma = \langle\chi|\sigma^{(0)}_{\rm el} + \sigma^{(1)}_{\rm el}|\chi\rangle, \tag{119}$$

and

$$\begin{aligned}
\sigma^{(0)}_{\rm el} &= \frac{\alpha^2}{3}\biggl[\langle\phi_{\rm el}|\sum_b \frac{1}{x_b}|\phi_{\rm el}\rangle + \langle\phi_{\rm el}|\sum_a \vec x_a\times\vec q_a \frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b \frac{\vec x_b\times\vec q_b}{x_b^3}|\phi_{\rm el}\rangle\biggr], && (120)\\
\sigma^{(1)}_{\rm n} &= \frac{\alpha^2}{3}\biggl[2\,\langle\phi_{\rm el}|\sum_b\frac{1}{x_b}\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\,\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle\\
&\quad +\langle\phi_{\rm el}|\sum_a \vec x_a\times\vec q_a\frac{1}{(\mathcal{E}-H_{\rm el})'}\,(\overset{\leftrightarrow}{H}_{\rm n} - \mathcal{E}_{\rm a})\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}|\phi_{\rm el}\rangle\\
&\quad +\langle\phi_{\rm el}|\,\overset{\leftrightarrow}{H}_{\rm n}\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_a\vec x_a\times\vec q_a\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}|\phi_{\rm el}\rangle\\
&\quad +\langle\phi_{\rm el}|\sum_a\vec x_a\times\vec q_a\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\,\overset{\leftrightarrow}{H}_{\rm n}\,|\phi_{\rm el}\rangle\biggr], && (121)\\
\sigma^{(1)}_{\rm d} &= -\frac{\alpha^2}{3\,g_A}\,\langle\phi_{\rm el}\biggl|\frac{(g_A-1)}{m_A}\sum_b\frac{\vec x_b}{x_b^3}\cdot(\vec x_{\rm el}+\vec R) - \frac{1}{m_B\,R}\biggr|\phi_{\rm el}\rangle, && (122)\\
\sigma^{(1)}_{\rm s} &= \frac{\alpha^2}{3\,g_A}\,\langle\phi_{\rm el}|\sum_a\vec x_a\times\vec q_a\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\biggl\{\frac{1}{m_A}\sum_b\frac{\vec x_b}{x_b^3}\times\Bigl[\vec P + (g_A-1)\,\vec q_{\rm el}\Bigr]\\
&\quad -\frac{\vec R}{R^3}\times\biggl[\frac{g_A}{m_B}\,\vec P + \frac{(g_A-1)}{m_A}\,(\vec P - \vec q_{\rm el})\biggr]\biggr\}|\phi_{\rm el}\rangle, && (123)\\
\sigma^{(1)}_{\rm l} &= \frac{\alpha^2}{3}\langle\phi_{\rm el}|\sum_b\frac{\vec x_b\times\vec q_b}{x_b^3}\,\frac{1}{(\mathcal{E}-H_{\rm el})'}\biggl[\frac{1}{m_A}\,(\vec x_{\rm el}+\vec R)\times(2\,\vec P - \vec q_{\rm el}) - \frac{1}{m_{\rm n}}\,\vec R\times\vec P\biggr]|\phi_{\rm el}\rangle && (124)
\end{aligned}$$

These formulae can be further simplified by shifting the reference frame to the geometrical center and by using gerade symmetry of the ground electronic state of H_2 and isotopomers.

VII. SUMMARY

We have presented a general approach to finite nuclear mass corrections in molecular properties which is based on NAPT [3]. These corrections were represented in terms of electronic matrix elements averaged with the nuclear wave function, similarly to that in the adiabatic approximation. We obtained formulae for nonadiabatic relativistic corrections which can be used to perform accurate calculations of dissociation and rovibrational energies. Currently the accuracy of theoretical predictions in H_2 [5] are limited by these not well known effects. Similarly, we obtained formulae for the nonadiabatic corrections to the transition electric dipole moment and the electric dipole polarizability. They can be used for the comparison with precise measurements of polarizabilities, for example in such complicated system as excited vibrational states of the water molecule [32, 33]. Finally, we presented nonadiabatic corrections to the magnetic shielding, which are important for molecules involving hydrogen or deuterium, where the finite nuclear mass significantly $\sim 10^{-3}$ affects the magnetic shielding.

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