RESEARCH ARTICLE

Nonadiabatic corrections to electric quadrupole transition rates in H_2

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ARTICLE HISTORY
Compiled January 22, 2026

ABSTRACT
We derive formulas and perform calculations of nonadiabatic corrections to rates of electric quadrupole transitions in the hydrogen molecule. These corrections can be represented in terms of a single curve $D^{(1)}(R)$, similarly to the Born-Oppenheimer one, $D^{(0)}(R)$, derived originally by Wolniewicz. Numerical results change E2 transition rates for the fundamental band by as much as 0.4 - 12% depending on rotational quantum numbers.

KEYWORDS
hydrogen; molecule; quadrupole; transition; nonadiabatic

1. Introduction

Most of the calculations of molecular properties are performed in the Born-Oppenheimer (BO) approximation. When higher precision is needed, e.g., for accurately measured transition energies in H_2 [1, 2, 3, 4], one includes adiabatic and nonadiabatic corrections. These corrections can be calculated systematically within the so-called nonadiabatic perturbation theory (NAPT) [6, 7]. Using NAPT, one can calculate not only corrections to rovibrational energies, but also to many other physical properties [8], like the nuclear magnetic shielding. This allowed for the most accurate determination of deuteron and triton magnetic moments [9].

In this work, we derive a formula for the leading nonadiabatic correction to rates of electric quadrupole transitions in H_2. This nonadiabatic correction can be represented in terms of a single function $D^{(1)}(R)$, which can be added to the BO quadrupole moment function $D^{(0)}(R)$, calculated by Wolniewicz in Ref. [10], recalculated by Komasa [11] using ECG functions, and significantly improved here using an enhanced version of H2SOLV code [12], which employs the Kołos-Wolniewicz (KW) functions. Apart from many applications in astrophysics, these accurate rates can be used in the primary thermometry for temperatures as low as 10 K [4, 13, 14, 5]. In particular Authors of Ref. [14] propose to measure the ratio of two transition rates from the same vibrational band to achieve higher accuracy for temperature due to cancellation of experimental and theoretical uncertainties. Hydrogen molecule is the best for this purpose, because

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transition rates can be calculated very accurately from first principles, and this work is the first step toward this accurate termometry.

2. Nonadiabatic perturbation theory

Following Ref. [8], let us start from a nonrelativistic Hamiltonian for a neutral diatomic molecule

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

where the summation index a enumerates all electrons, and A and B refer to nuclei, and atomic units are used throughout the paper. 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 subsequently change variables to $\{\vec{R},\, \vec{R}_G,\, \vec{x}_a\}$ according to

$$\vec{r}_A = \vec{R}_G + \epsilon_B\,\vec{R}, \tag{2}$$

$$\vec{r}_B = \vec{R}_G - \epsilon_A\,\vec{R}, \tag{3}$$

$$\vec{r}_a = \vec{R}_G + \vec{x}_a, \tag{4}$$

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

$$\vec{p}_A = \epsilon_A\,\vec{P}_G + \vec{P} - \epsilon_A \sum_a \vec{q}_a, \tag{5}$$

$$\vec{p}_B = \epsilon_B\,\vec{P}_G - \vec{P} - \epsilon_B \sum_a \vec{q}_a, \tag{6}$$

$$\vec{p}_a = \vec{q}_a, \tag{7}$$

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 $\phi = \phi(\vec{x}_a,\, \vec{R})$. We now choose the center of the reference frame at the nuclear mass center,

$$\epsilon_A = \frac{m_A}{m_A + m_B}, \qquad \epsilon_B = \frac{m_B}{m_A + m_B}\,, \tag{8}$$

and split the Hamiltonian into the electronic and nuclear parts,

$$H = H_{\rm el} + H_{\rm n}, \tag{9}$$

$$H_{\rm el} = \sum_a \frac{\vec{q}_a^{\,2}}{2\,m} + V, \tag{10}$$

$$H_{\rm n} = \left(\frac{1}{2\,m_A} + \frac{1}{2\,m_B}\right)\vec{P}^{\,2} + \frac{1}{2\,(m_A + m_B)}\left(\sum_a \vec{q}_a\right)^2 = H'_{\rm n} + H''_{\rm n}. \tag{11}$$

This form of the nuclear Hamiltonian is convenient for the calculation of nonadiabatic effects.

Next, the total angular momentum operator $\vec{J}$ does not depend on the reference point, because we assumed the vanishing total momentum for molecular states. Therefore we chose for convenience $\vec{R}_G$ as a reference point and J becomes

$$\vec{J} = \sum_a (\vec{r}_a - \vec{R}_G) \times \vec{p}_a + (\vec{r}_A - \vec{R}_G) \times \vec{p}_A + (\vec{r}_B - \vec{R}_G) \times \vec{p}_B\,. \tag{12}$$

In new variables

$$\vec{J} = \sum_a \vec{x}_a \times \vec{q}_a + \vec{R} \times \vec{P} \equiv \vec{J}_{\rm el} + \vec{J}_{\rm n}, \tag{13}$$

J can also be split into electronic $\vec{J}_{\rm el}$ and nuclear $\vec{J}_{\rm n}$ parts.

Let us now introduce NAPT [6, 7]. The total nonrelativistic wave function ϕ of an arbitrary molecule is the solution of the stationary Schrödinger equation

$$[H - E]\,|\phi\rangle = 0\,, \tag{14}$$

with the Hamiltonian H being a sum of the electronic $H_{\rm el}$ and nuclear $H_{\rm n}$ parts, Eq. (11). In the adiabatic approximation the wave function $\phi = \phi_{\rm a}$, where

$$\phi_{\rm a}(\vec{x}, \vec{R}) = \phi_{\rm el}(\vec{x})\;\chi(\vec{R}), \tag{15}$$

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 parametrically on the nuclear relative coordinate $\vec{R}$. The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

$$\big[H_{\rm el} - \mathcal{E}_{\rm el}(R)\big]\,|\phi_{\rm el}\rangle = 0, \tag{16}$$

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

$$\big[H_{\rm n} + \mathcal{E}_{\rm a}(R) + \mathcal{E}_{\rm el}(R) - E_{\rm a}\big]\,|\chi\rangle = 0\,, \tag{17}$$

where the adiabatic correction $\mathcal{E}_{\rm a}(R)$ is

$$\mathcal{E}_{\rm a}(R) = \big\langle \phi_{\rm el} | H_{\rm n} | \phi_{\rm el} \big\rangle_{\rm el}\,. \tag{18}$$

In NAPT, the total wave function is the sum of the adiabatic solution and a nonadiabatic correction

$$\phi = \phi_{\rm a} + \delta\phi_{\rm na} = \phi_{\rm el}\,\chi + \delta\phi_{\rm na}\,. \tag{19}$$

The nonadiabatic correction $\delta\phi_{\rm na}$ is decomposed into two parts,

$$\delta\phi_{\rm na} = \phi_{\rm el}\,\delta\chi + \delta'\phi_{\rm na}\,, \tag{20}$$

obeying the following orthogonality conditions

$$\langle \delta' \phi_{\rm na} | \phi_{\rm el} \rangle_{\rm el} = 0\,, \tag{21}$$

$$\langle \delta\chi | \chi \rangle = 0\,, \tag{22}$$

which imply the normalization condition $\langle \phi_a | \phi \rangle = 1$. In the first order of NAPT one has

$$|\delta' \phi_{\rm na}\rangle^{(1)} = \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, H_{\rm n}\, |\phi_{\rm el}\, \chi\rangle, \tag{23}$$

where $1/(\mathcal{E}_{\rm el} - H_{\rm el})'$ denotes the resolvent with the reference state $\phi_{\rm el}$ subtracted out. This correction to the wave function can be used to derive the finite nuclear mass corrections to various matrix elements. Consider the Hermitian electronic operator Q (without derivatives with respect to nuclear variables) and its matrix element between (different) rovibrational states. In the BO approximation, this matrix element can be represented in terms of the diagonal electronic matrix element nested in the nuclear matrix element, namely

$$\langle Q \rangle^{(0)} \equiv \langle \phi_{\rm el}\, \chi_{\rm f} | Q | \phi_{\rm el}\, \chi_{\rm i} \rangle = \langle \chi_{\rm f} | \langle Q \rangle^{(0)}_{\rm el} | \chi_{\rm i} \rangle, \tag{24}$$

where

$$\langle Q \rangle^{(0)}_{\rm el} \equiv \langle Q \rangle_{\rm el} = \langle \phi_{\rm el} | Q | \phi_{\rm el} \rangle. \tag{25}$$

We will show that the same holds for the leading nonadiabatic corrections, which is

$$\langle Q \rangle^{(1)} = \langle \phi_{\rm el}\, \chi_{\rm f} | H_{\rm n}\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, Q | \phi_{\rm el}\, \chi_{\rm i} \rangle + \langle \phi_{\rm el}\, \chi_{\rm f} | Q\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, H_{\rm n} | \phi_{\rm el}\, \chi_{\rm i} \rangle. \tag{26}$$

Namely,

$$\begin{aligned} \langle Q \rangle^{(1)} = & \int d^3R \biggl\{ (\chi_{\rm f}^*\, \chi_{\rm i}) \biggl[\langle H_{\rm n}\, \phi_{\rm el} | \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, Q\, |\phi_{\rm el}\rangle + \langle \phi_{\rm el} | Q\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, |H_{\rm n}\, \phi_{\rm el}\rangle \biggr] \\ & - \frac{\vec\nabla\bigl(\chi_{\rm f}^*\, \chi_{\rm i}\bigr)}{2\, m_{\rm n}} \biggl[\langle \vec\nabla_R \phi_{\rm el} | \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, Q\, |\phi_{\rm el}\rangle + \langle \phi_{\rm el} | Q\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, |\vec\nabla_R \phi_{\rm el}\rangle \biggr] \\ & - \frac{\Bigl(\chi_{\rm i}\, \vec\nabla \chi_{\rm f}^* - \chi_{\rm f}^*\, \vec\nabla \chi_{\rm i}\Bigr)}{2\, m_{\rm n}} \biggl[\langle \vec\nabla_R \phi_{\rm el} | \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, Q\, |\phi_{\rm el}\rangle - \langle \phi_{\rm el} | Q\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, |\vec\nabla_R \phi_{\rm el}\rangle \biggr] \biggr\}. \end{aligned} \tag{27}$$

Assuming Q is invariant with respect to time reversal, the third term vanishes, and with the help of integration by parts, we obtain

$$\langle Q \rangle^{(1)} = \langle \chi_{\rm f} | \langle Q \rangle^{(1)}_{\rm el} | \chi_{\rm i} \rangle, \tag{28}$$

$$\langle Q \rangle^{(1)}_{\rm el} = \langle \phi_{\rm el} |\, \overset{\leftrightarrow}{H}_{\rm n}\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, Q\, |\phi_{\rm el}\rangle + \langle \phi_{\rm el} |\, Q\, \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\, \overset{\leftrightarrow}{H}_{\rm n}\, |\phi_{\rm el}\rangle, \tag{29}$$

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

$$\langle\psi'_{\rm el}|\overset{\leftrightarrow}{H}_{\rm n}|\psi_{\rm el}\rangle = \langle\vec\nabla_R\,\psi'_{\rm el}|\vec\nabla_R\,\psi_{\rm el}\rangle/(2\,m_{\rm n}) + \langle\psi'_{\rm el}|H''_{\rm n}|\psi_{\rm el}\rangle, \tag{30}$$

and where $m_{\rm n}$ is the reduced nuclear mass.

3. Electric quadrupole moment

The electric quadrupole moment operator is

$$D^{ij} = \sum_\alpha e_\alpha\,(r^i_{\alpha M}\,r^j_{\alpha M} - r^2_{\alpha M}\,\delta^{ij}/3)\,, \tag{31}$$

where the summation index α refers to both electrons and nuclei, e_α refers to the electric charge of the α-th particle, and $\vec r_{\alpha M}$ are particle positions with respect to the center of mass, $\vec r_M$,

$$\vec r_M = \sum_\alpha \frac{m_\alpha\,\vec r_\alpha}{M}\,. \tag{32}$$

For the hydrogen molecule, $\sum_\alpha e_\alpha = 0$, and $M_A = M_B = m_N$, so the total mass M is

$$M = 2\,m_N + 2\,m\,. \tag{33}$$

Let us rewrite the quadrupole moment operator in terms of position vectors $\vec x_a = \vec r_{aG}$ with respect to the geometric center $\vec r_G$, which coincides with the nuclear mass center.

$$\vec r_G = (\vec r_A + \vec r_B)/2. \tag{34}$$

Namely

$$\vec x_G = \vec r_G - \vec r_M = \sum_\alpha \frac{m_\alpha}{M}\,\vec r_G - \sum_\alpha \frac{m_\alpha\,\vec r_\alpha}{M} = -\sum_\alpha \frac{m_\alpha\,\vec r_{\alpha G}}{M}. \tag{35}$$

Because $\vec r_G$ is the geometric center, the sum over nuclei cancels out, and

$$\vec x_G = -\frac{m}{M}\,\vec r_{\rm el}\,, \tag{36}$$

where

$$\vec r_{\rm el} = \sum_a \vec r_{aG}\,. \tag{37}$$

The quadrupole moment operator in new variables becomes

$$D^{ij} = \sum_\alpha e_a\left[(r^i_{\alpha G} + x^i_G)\,(r^j_{\alpha G} + x^j_G) - (\vec r_{\alpha G} + \vec x_G)^2\,\frac{\delta^{ij}}{3}\right]$$

$$= D_G^{ij} + D_G^i\,x_G^j + x_G^i\,D_G^j - 2\,\vec{D}_G\,\vec{x}_G\,\frac{\delta^{ij}}{3} + O\biggl(\frac{m}{m_N}\biggr)^2 \tag{38}$$

where, assuming e is the electron charge,

$$D_G^i = \sum_\alpha e_\alpha\,r_{\alpha G}^i = e\,r_{\rm el}^i \tag{39}$$

and

$$D_G^{ij} = \sum_\alpha e_\alpha \left(r_{\alpha G}^i\,r_{\alpha G}^j - \vec{r}_{\alpha G}^{\,2}\,\frac{\delta^{ij}}{3}\right) = e\,r_{\rm el}^{ij} - \frac{e}{2}\left(R^i\,R^j - \vec{R}^{\,2}\,\frac{\delta^{ij}}{3}\right) \tag{40}$$

with

$$r_{\rm el}^{ij} \equiv \sum_a \left(r_{aG}^i\,r_{aG}^j - \vec{r}_{aG}^{\,2}\,\frac{\delta^{ij}}{3}\right). \tag{41}$$

The quadrupole moment operator is therefore

$$D^{ij} = e\,r_{\rm el}^{ij} - \frac{e}{2}\left(R^i\,R^j - \vec{R}^{\,2}\,\frac{\delta^{ij}}{3}\right) - e\,\frac{m}{m_N}\left(r_{\rm el}^i\,r_{\rm el}^j - \vec{r}_{\rm el}^{\,2}\,\frac{\delta^{ij}}{3}\right) + O\biggl(\frac{m}{m_N}\biggr)^2. \tag{42}$$

Its matrix element on the $\phi_{\rm el}$ state in the BO approximation is

$$D_{\rm el}^{(0)ij} = e\left(n^i\,n^j - \frac{\delta^{ij}}{3}\right)D^{(0)}(R) \tag{43}$$

where $n^i \equiv R^i/R$ and

$$D^{(0)}(R) = \frac{3}{2}\left[\bigl\langle r_{\rm el}^{ij}\,n^i\,n^j\bigr\rangle - \frac{R^2}{3}\right], \tag{44}$$

while the leading nonadiabatic correction is

$$D_{\rm el}^{(1)ij} = -\,e\,\frac{m}{m_N}\left\langle r_{\rm el}^i\,r_{\rm el}^j - \vec{r}_{\rm el}^{\,2}\,\frac{\delta^{ij}}{3}\right\rangle + 2\,e\left\langle r_{\rm el}^{ij}\,\frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,\overset{\leftrightarrow}{H}_{\rm n}\right\rangle. \tag{45}$$

Let us denote

$$|\phi_{\rm el}^{ij}\rangle = \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})'}\,r_{\rm el}^{ij}|\phi_{\rm el}\rangle\,, \tag{46}$$

$$|\phi_\Pi^k\rangle = \frac{1}{(\mathcal{E}_{\rm el} - H_{\rm el})}\,\sum_a (\vec{n}\cdot\vec{r}_a)\,r_{a\perp}^k|\phi_{\rm el}\rangle\,, \tag{47}$$

$$|\phi_{\Sigma^+}\rangle = n^i\,n^j\,|\phi_{\rm el}^{ij}\rangle\,. \tag{48}$$

Then, with reduced mass $m_{\rm n} = m_N/2$ the adiabatic correction to the quadrupole moment becomes

$$D^{(1)ij}_{\rm el} = e\,\frac{m}{m_{\rm n}}\,\bigl(n^i\,n^j - \delta^{ij}/3\bigr)\,D^{(1)}(R)\,, \tag{49}$$

where

$$D^{(1)}(R) = \frac{3}{2}\left[-\frac{1}{2}\left\langle(\vec r_{\rm el}\cdot\vec n)^2 - \frac{\vec r_{\rm el}^{\,2}}{3}\right\rangle + \frac{1}{m}\,\langle n^i\,n^j\,\nabla^k_R\phi^{ij}_{\rm el}|\nabla^k_R\phi_{\rm el}\rangle + \frac{1}{4\,m}\,\langle\phi_{\Sigma^+}|\vec p_{\rm el}^{\,2}|\phi_{\rm el}\rangle\right], \tag{50}$$

and where $\vec p_{\rm el} = \sum_a \vec q_a$. Since

$$n^i\,n^j\,\nabla^k = -\frac{n^i}{R}\,\bigl(\delta^{kj} - n^k\,n^j\bigr) - \frac{n^j}{R}\,\bigl(\delta^{ki} - n^k\,n^i\bigr) + \nabla^k\,n^i\,n^j\,. \tag{51}$$

Then

$$\langle n^i\,n^j\,\nabla^k_R\phi^{ij}_{\rm el}|\nabla^k_R\phi_{\rm el}\rangle = \frac{1}{m}\langle\nabla^k_R\phi_{\Sigma^+}|\nabla^k_R\phi_{\rm el}\rangle - \frac{2}{m\,R}\,\langle\phi^k_\Pi|\nabla^k_R\phi_{\rm el}\rangle\,. \tag{52}$$

The last term in the above can be transformed using

$$\vec\nabla_R = \vec n\,(\vec n\cdot\vec\nabla_R) - \vec n\times(\vec n\times\vec\nabla_R), \tag{53}$$

to the form

$$\langle\vec\phi_\Pi|\vec\nabla_R\phi_{\rm el}\rangle = -\,\langle\vec\phi_\Pi|\vec n\times(\vec n\times\vec\nabla_R)|\phi_{\rm el}\rangle = -\frac{i}{R}\,\langle\vec\phi_\Pi|\vec n\times\vec J_{\rm n}|\phi_{\rm el}\rangle = \frac{i}{R^2}\,\langle\vec\phi_\Pi|\vec R\times\vec J_{\rm el}|\phi_{\rm el}\rangle\,. \tag{54}$$

Thus, we have obtained the following formulas for the quadrupole moment in H_2 (in atomic units).

$$D(R) = D^{(0)}(R) + \frac{m}{m_{\rm n}}\,D^{(1)}(R) \tag{55}$$

$$D^{(0)}(R) = \frac{3}{2}\,Q_0(R) \tag{56}$$

$$D^{(1)}(R) = \frac{3}{2}\,\bigl[Q_1(R) + Q_2(R) + Q_3(R) + Q_4(R)\bigr], \tag{57}$$

where

$$Q_0(R) = \sum_a\left\langle\phi_{\rm el}\left|(\vec n\cdot\vec r_a)^2 - \frac{\vec r_a^{\,2}}{3}\right|\phi_{\rm el}\right\rangle - \frac{R^2}{3}, \tag{58}$$

$$Q_1(R) = -\frac{1}{2}\left\langle\phi_{\rm el}\left|(\vec r_{\rm el}\cdot\vec n)^2 - \frac{\vec r_{\rm el}^{\,2}}{3}\right|\phi_{\rm el}\right\rangle, \tag{59}$$

$$Q_2(R) = \langle\nabla^k_R\phi_{\Sigma^+}|\nabla^k_R\phi_{\rm el}\rangle\,, \tag{60}$$

$$Q_3(R) = -\frac{2\,i}{R^3}\langle\vec\phi_\Pi|\vec R\times\vec J_{\rm el}|\phi_{\rm el}\rangle, \tag{61}$$

$$Q_4(R) = \frac{1}{4}\,\langle\phi_{\Sigma^+}|\Big(\sum_a \vec{p}_a\Big)^2|\phi_{\rm el}\rangle. \tag{62}$$

This is the complete formula for the leading nonadiabatic correction to the quadrupole moment in a homonuclear diatomic molecule. The second term involves differentiation over the nuclear variable $\vec{R}$, and the following section describes a convenient way to calculate it with high precision.

4. *R*-derivatives

Following Ref. [15], let us now explain how one can calculate R-derivatives in the exponential basis. Let ψ_k be the k-th element of the basis set employed to expand the ground-state electronic wave function

$$\phi_{\rm el} = \sum_k v_k\,\psi_k\,, \tag{63}$$

and let $\vec{v}$ be a vector consisting of real coefficients of this expansion. The adiabatic correction can be written as

$$\big\langle\vec{\nabla}_R\phi_{\rm el}\big|\vec{\nabla}_R\phi_{\rm el}\big\rangle = \sum_{k,l} v_k\,v_l\,\big\langle\vec{\nabla}_R\psi_k\big|\vec{\nabla}_R\psi_l\big\rangle + \partial_R v_k\,\partial_R v_l\,\big\langle\psi_k\big|\psi_l\big\rangle + 2\,\partial_R v_k\,v_l\,\big\langle\psi_k\big|\partial_R\psi_l\big\rangle\,, \tag{64}$$

where we assume that nonlinear parameters do not depend on R. Next, let us define the following matrices

$$\begin{aligned}\mathcal{H}_{kl} &= \big\langle\psi_k\big|H_{\rm el}\psi_l\big\rangle\,, &(65)\\ \mathcal{N}_{kl} &= \big\langle\psi_k\big|\psi_l\big\rangle\,, &(66)\\ \mathcal{A}_{kl} &= \big\langle\psi_k\big|\partial_R\psi_l\big\rangle\,, &(67)\\ \mathcal{B}_{kl} &= \big\langle\vec{\nabla}_R\psi_k\big|\vec{\nabla}_R\psi_l\big\rangle\,. &(68)\end{aligned}$$

With this notation, the electronic Schrödinger equation can be written in the matrix form as

$$(\mathcal{H} - \mathcal{E}_{\rm el}\,\mathcal{N})\,\vec{v} = 0\,. \tag{69}$$

Let us further consider the first-order R-derivative of $\phi_{\rm el}$

$$\partial_R\phi_{\rm el} = \sum_k\left(\psi_k\,\partial_R v_k + v_k\,\partial_R\psi_k\right)\,. \tag{70}$$

The term $\partial_R\psi_k$ is assumed to be known, as it is the derivative of a basis function at constant values of nonlinear parameters. The derivative $\partial_R v_k$ can be obtained by taking the derivative of Eq. (69), namely

$$(\mathcal{H} - \mathcal{E}_{\rm el}\,\mathcal{N})\,\partial_R\vec{v} + (\partial_R\mathcal{H} - \partial_R\mathcal{E}_{\rm el}\,\mathcal{N} - \mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\,\vec{v} = 0, \tag{71}$$

so that

$$\partial_R \vec{v} = \frac{1}{(\mathcal{E}_{\rm el}\,\mathcal{N}-\mathcal{H})'}\,(\partial_R\mathcal{H}-\mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\,\vec{v}-\frac{1}{2}\,\vec{v}\,\left(\vec{v}^T\,\partial_R\mathcal{N}\,\vec{v}\right)\,, \tag{72}$$

where the last term was obtained by differentiation of the normalization condition

$$\vec{v}^T\,\mathcal{N}\,\vec{v} = 1 \tag{73}$$

leading to

$$2\,(\partial_R\vec{v})^T\,\mathcal{N}\,\vec{v}+\vec{v}^T\,\partial_R\mathcal{N}\,\vec{v} = 0\,. \tag{74}$$

Now, the adiabatic correction of Eq. (64) is transformed to the form

$$\langle\nabla_R^k\phi_{\rm el}|\nabla_R^k\phi_{\rm el}\rangle = \vec{v}^T\,\mathcal{B}\,\vec{v}+(\partial_R\vec{v})^T\,\mathcal{N}\,\partial_R\vec{v}+2\,(\partial_R\vec{v})^T\,\mathcal{A}\,\vec{v}\,. \tag{75}$$

To calculate Q_2, which contains R-derivatives, we define

$$\delta H = \xi\,n^i\,n^j\,r_{\rm el}^{ij} \tag{76}$$

and add it to the nonrelativistic Hamiltonian $H_{\rm el}$. So that $Q_2(R)$ can be obtained by a differentiation in ξ,

$$Q_2 = \frac{1}{2}\,\frac{d}{d\,\xi}\bigg|_{\xi=0}\langle\nabla_R^k\phi_{\rm el}|\nabla_R^k\phi_{\rm el}\rangle_\xi\,, \tag{77}$$

where the subscript ξ in $\langle\ldots\rangle_\xi$ stands for the ξ-dependence of $\phi_{\rm el}$ due to ξ-dependence of the Hamiltonian in Eq. (76). The methods for calculation of Q_2 are described in the next Section and in Appendix A.

5. Numerical calculations

[Table 1 about here.]

Following Ref. [16] we employ a variational approach to obtain $\phi_{\rm el}$ for the ground electronic Σ^+ state and utilize explicitly correlated exponential functions with polynomial dependence on interparticle distances of the form [17]

$$\Phi_{\{n\}} \;=\; e^{-y\,\eta_1-x\,\eta_2-u\,\xi_1-w\,\xi_2}\,r_{12}^{n_0}\,\eta_1^{n_1}\,\eta_2^{n_2}\,\xi_1^{n_3}\,\xi_2^{n_4}, \tag{78}$$

where η_i and ξ_i are proportional to confocal elliptic coordinates and are given by $\eta_i = r_{iA}-r_{iB}$, $\xi_i = r_{iA}+r_{iB}$, with i enumerating electrons and real y, x, u, w nonlinear parameters subject to variational minimization. By $\{n\}$ we denote an ordered set of interparticle coordinate exponents, $(n_0, n_1, n_2, n_3, n_4)$, which are conventionally restricted by a shell parameter Ω,

$$\sum_{j=0}^{4} n_j \le \Omega\,. \tag{79}$$

If a symmetry restriction is imposed, the set of allowed $\{n\}$ is constrained even further for special values of nonlinear parameters. By construction, the trial functions depend on two-electron coordinates and account for the correlation via explicit dependence on the coordinate r_{12}. The electronic wavefunction is represented as

$$\Psi_{\Sigma^+} = \sum_{\{n\}} v_{\{n\}} \hat{S}^+_{AB} \hat{S}^+_{12} \Phi_{\{n\}}, \tag{80}$$

$$\Psi_\Pi = \sum_{\{n\}} v_{\{n\}} \hat{S}^-_{AB} \hat{S}^+_{12}\, r^i_{1\perp}\, \Phi_{\{n\}}\,, \tag{81}$$

where $r^i_\perp = r^i - n^i\, \vec{n}\, \vec{r}$, $\hat{S}^\pm_{AB} = 1 \pm P_{AB}$ and P_{AB} permutes the nuclei A and B, $\hat{S}^\pm_{12} = 1 \pm P_{12}$ and P_{12} interchange the two electrons, and appropriate $\pm$ signs are chosen to fulfill the symmetry criteria for *gerade/ungerade* and *singlet/triplet* states. By solving the secular equation one obtains linear coefficients $v_{\{n\}}$. Such a form of wavefunction expansion is commonly referred to as the Kołos-Wolniewicz basis [17]. In our calculations we use two specific cases of the KW basis, namely the symmetric James-Coolidge (JC) basis ($y = x = 0, \alpha = u = w$) for $R \le 10$ au and symmetric Heitler-London (HL) basis ($\alpha = -y = x = u = w$) for $R \ge 10$ au. Consequently, the resulting parametrization of our trial basis is extremely compact – just a single nonlinear parameter α and the integer shell constraint Ω.

Matrix elements with KW functions can be expressed as a linear combination of f-integrals with various sets of $\{n\}$, which are defined as

$$f_{\{n\}}(R) = R \int \frac{d^3 r_1}{4\,\pi} \int \frac{d^3 r_2}{4\,\pi}\, \frac{e^{-w_1\, r_{12} - u\, \xi_1 - w\, \xi_2 - y\, \eta_1 - x\, \eta_2}}{r_{1A}\, r_{1B}\, r_{2A}\, r_{2B}}\, r_{12}^{n_0 - 1} \eta_1^{n_1} \eta_2^{n_2} \xi_1^{n_3} \xi_2^{n_4}. \tag{82}$$

This is because all matrix elements can be expressed in terms of interparticle distances and their derivatives. For example, Q_0 and Q_1 can be written as the following expectation values

$$Q_0 = -\frac{1}{6}\, \langle R^2 + r_{1A}^2 + r_{1B}^2 + r_{2A}^2 + r_{2B}^2 \rangle + \frac{1}{4\,R^2}\, \langle (r_{1A}^2 - r_{1B}^2)^2 + (r_{2A}^2 - r_{2B}^2)^2 \rangle\,, \tag{83}$$

$$Q_1 = \frac{1}{8\,R^2}\, \langle (r_{1A}^2 - r_{1B}^2 + r_{2A}^2 - r_{2B}^2)^2 \rangle + \frac{1}{6}\, \langle r_{1A}^2 + r_{1B}^2 + r_{2A}^2 + r_{2B}^2 - R^2 - r_{12}^2 \rangle. \tag{84}$$

The efficient recursive evaluation of f-integrals in arbitrary (extended) precision is described in Refs. [12, 18]. The numerical algebra part of the calculations is performed using parallel `HSL_mp54` Cholesky solver [19, 20] adapted to quad-double arithmetic precision (64 decimal digits) [21].

The other operators Q_2, Q_3, and Q_4 are second-order matrix elements and thus require the construction of intermediate states,

$$|\phi_{\Sigma^+}\rangle = \frac{1}{(\mathcal{E}_\mathrm{el} - H_\mathrm{el})'}\, r_\mathrm{el}^{ij} n^i\, n^j |\phi_\mathrm{el}\rangle\,, \tag{85}$$

$$|\phi^k_\Pi\rangle = \frac{1}{(\mathcal{E}_\mathrm{el} - H_\mathrm{el})'} \sum_a (\vec{n} \cdot \vec{r}_a)\, r^k_{a\perp} |\phi_\mathrm{el}\rangle\,, \tag{86}$$

which are obtained by solving a corresponding linear equation in the basis of Ψ_{Σ^+} and Ψ_Π functions, respectively. Those bases for intermediate states carry exactly the same set of nonlinear parameters as the external basis – optimized for the energy of the ground electronic state. This considerably reduces the number of integrals that have to be computed, and for the case of $|\phi_{\Sigma^+}\rangle$ allows us to reuse the basis already constructed for the external (ground) state, hence we have $\Omega_{\Sigma^+} = \Omega$. Whereas for $|\phi^k_\Pi\rangle$ we choose $\Omega_\Pi = \Omega - 2$, which curiously, due to different symmetry restrictions for Σ_g^+ and Π_g, results in almost the same basis sizes, both in JC and HL cases.

Out of all $Q_i(R)$, the calculation of Q_2 in Eq. (77) is the most difficult. The simplest way to evaluate it is to perform the differentiation in ξ numerically,

$$Q_2 \approx \frac{1}{2}\,\frac{\langle\nabla^k_R\phi_{\rm el}|\nabla^k_R\phi_{\rm el}\rangle_\xi - \langle\nabla^k_R\phi_{\rm el}|\nabla^k_R\phi_{\rm el}\rangle_{-\xi}}{2\,\xi} \tag{87}$$

The matrix element $\langle\nabla^k_R\phi_{\rm el}|\nabla^k_R\phi_{\rm el}\rangle_\xi$ is constructed according to Eq. (75), which requires solving for a new eigenpair for each ξ, due to the ξ-dependence of the Hamiltonian. Already with $\xi = 10^{-5}$, this numerical method yields accurate results ($\delta \approx -2.5\cdot 10^{-7}$ at $R = 1.4011$ au) in comparison to the method based on analytical ξ-differentiation, described in Appendix A. This confirms that the accuracy of this method is limited by the basis size, rather than the numerical differentiation at $\xi = 0$.

[Figure 1 about here.]

Numerical results for $D^{(0)}$ and $D^{(1)}$ are presented in Table A1 and in Fig. A1. These results have been obtained with a single sector JC basis ($\Omega = 15, 16$) for $R \leq 10$ and a HL basis ($\Omega = 13, 14$) for $R \geq 10$. Individual contributions $Q_i(R)$ to $D^{(0)}(R)$ and $D^{(1)}(R)$ are presented in Supplementary Material [23]. The relative accuracy of both $D^{(0)}(R)$ and $D^{(1)}(R)$ is typically no worse than 10^{-9} and becomes especially high ($\sim 10^{-17}$) for $D^{(0)}(R)$ at large R, proving that a simple single-sector HL basis is an excellent choice for this purpose.

As expected, the quadrupole moment and its finite nuclear mass correction vanish as $R \to 0$. Even more important, and a stringent test of our calculations, is the long-range asymptotics. Although each of the individual parts, Q_1, $Q_2 + Q_3$, and Q_4, has a leading $1/R^3$ term, those leading terms cancel out in the total sum. Because the long-range asymptotics of $D^{(0)}(R)$ is $1/R^6$, see Supplementary Material [23], one may expect a similar asymptotics for $D^{(1)}(R)$, and indeed this is the case; see the bottom panel of Fig. A1.

Comparing to the previous calculations, Wolniewicz [10] defines $Q(R)$ by

$$Q(R) = \langle\phi_{\rm el}|\sum_a r_a^2\,\frac{3\,\cos^2(\theta_a) - 1}{2}|\phi_{\rm el}\rangle\,. \tag{88}$$

Nevertheless, his numerical values correspond to the following definition

$$Q(R) = \langle\phi_{\rm el}|\sum_a r_a^2\,[1 - 3\,\cos^2(\theta_a)]|\phi_{\rm el}\rangle + R^2 = -2\,D^{(0)}(R)\,. \tag{89}$$

For example, his result for $R = 1$ is 0.512 611 56, which is nearly -2 times our result $D^{(0)}(1) = -0.256\,305\,639\,0(5)$. Komasa in Ref. [11] defines $Q(R)$ with the opposite sign,

$$Q(R) = \langle\phi_{\rm el}|\sum_a r_a^2\,\frac{1-3\,\cos^2(\theta_a)}{2}|\phi_{\rm el}\rangle + \frac{R^2}{2} = -D^{(0)}(R) \tag{90}$$

and obtains $Q(1) = 0.256\,305\,641$. We have found that aside from this prefactor, the numerical results of Wolniewicz [10] and Komasa [11] are in agreement with ours.

6. Transition rates

Following the notation from Ref. [10], the spontaneous electric quadrupole transition probabilities from a (higher) initial state $v'J'$ to a (lower) final state $v''J''$, in atomic units, is given by (see Supplementary Material [23])

$$A_{\rm E2} = (4\,\pi R_\infty c)\,\frac{\alpha^5}{15}\,(E_{v'J'} - E_{v''J''})^5\,\langle v''J''|D(R)|v'J'\rangle^2\,f(J',J'')\,, \tag{91}$$

where R_∞ is the Rydberg constant, and rotational intensity factors are given by

$$f(J',J'') = \begin{cases} \dfrac{3(J'+1)(J'+2)}{2(2J'+1)(2J'+3)}, & J''=J'+2\ ({\rm O}) \\ \dfrac{J'(J'+1)}{(2J'-1)(2J'+3)}, & J''=J'\ ({\rm Q}) \\ \dfrac{3J'(J'-1)}{2(2J'-1)(2J'+1)}, & J''=J'-2\ ({\rm S}) \end{cases} \tag{92}$$

and satisfy the identity

$$f(J',J'+2) + f(J',J') + f(J',J'-2) = 1\,. \tag{93}$$

We note that Eq. (4) of Ref. [10] contains a misprint in the $J'' = J' + 2$ case, namely the numerator should read $3(J'+1)(J'+2)$ instead of $(3J'+1)(J'+2)$. Nevertheless, numerical transition rates in Ref. [10] appear to be calculated with the correct rotational factors.

The radial matrix element in Eq. (91) is calculated with $D(R)$ given by Eq. (55) and with nuclear wavefunctions χ being a solution of the radial equation with the inclusion of the diagonal adiabatic correction. We note that the $A_{\rm E2}$ rate is sensitive to this transition energy; therefore, we take values from the H2Spectre code [24], which are accurate to about 1 MHz. Our numerical results are in agreement with those of Wolniewicz [10] and Komasa [11], but should be more accurate due to the inclusion of the leading nonadiabatic correction $D^{(1)}$. In fact, the E2 transition rates' uncertainty is now dominated by the unknown relativistic corrections, which we estimated by α^2 times $A_{\rm E2}$. We note, that magnetic dipole (M1) transitions occur at the same wavelengths as the electric quadrupole (E2) transitions. Consequently, in the spontaneous emission the total transition probability is the sum of the separate M1 and E2 rates. Therefore, whenever transition rates in the Q-branch ($J'' = J'$) are of interest, one has to include also the M1 channel. For the M1 transition rates in Table A2, we use Eq. (13) from Ref. [11], and our results are in a good agreement.

In Table A2, apart from $A_{\rm M1}$, we present the $A^{Q}_{\rm E2}$, $A^{S}_{\rm E2}$, and $A^{O}_{\rm E2}$ transition rates for the Q ($J'' = J'$), S ($J'' = J' - 2$), and O ($J'' = J' + 2$) branches of the fundamental ($\nu = 1 \to 0$) band of H_2, respectively.

[Table 2 about here.]

In the Q-branch, we note that except for $J' = 1$, the magnetic dipole $A_{\rm M1}$ rate exceeds the nonadiabatic corrections to $A^{Q}_{\rm E2}$, significantly grows with J', and starting from $J' = 18$ exceeds the total $A^{Q}_{\rm E2}$. In the ($v = 1 \to 0$) O-branch, the relative nonadiabatic correction is nearly constant and amounts to $\approx 0.4\%$, the rapid drop in the magnitude of the overall E2 rate (as J' is increased) in this branch can be attributed to the strong suppression by the $(E_{v'J'} - E_{v''J''})^5$ factor in Eq. (91) as the energy difference goes to zero around $J' = 21$. Whereas for the S-branch, the relative nonadiabatic correction varies strongly, starting from $\approx 0.45\%$ at $J' = 2$, achieving a maximum of 12% at $J' = 15$ due to the smallness of the radial matrix element. This behaviour might be interesting to verify experimentally.

7. Summary

We have derived formulas for nonadiabatic corrections to electric quadrupole transitions in H_2 using NAPT. These corrections can be represented in terms of a single function $D^{(1)}(R)$, which is to be added to the BO function $D^{(0)}(R)$. We have performed numerical calculations of $D^{(0)}$ and $D^{(1)}$ using James-Coolidge and Heitler-London basis functions. Results for $D^{(0)}$ are in agreement with previous ones [10, 11], but are much more accurate and in the much wider range $R \leq 50$ a.u. Moreover, we have found that the long-range asymptotics of $D^{(1)}(R)$ is $\sim R^{-6}$, similarly to $D^{(0)}(R)$.

Using $D^{(0)}(R)$ and $D^{(1)}(R)$ curves, we have performed exemplary calculations of electric quadrupole transition rates in the $v = 1 \to 0$ band for $J'' = J', J' \pm 2$, and observed that nonadiabatic corrections to the Q- and O- branches are about 0.44% - 1.14%, which are a few to ten times larger than could be expected from a simple mass scaling by a factor of $m_e/m_{\rm n}$. In the S-branch at $J' = 15$, where the rate is as small as $5 \cdot 10^{-10}\, s^{-1}$, the nonadiabatic corrections raise the rate by as much as 12%.

With the improved quadrupole moment curve, one may recalculate all transition rates and lifetimes of H_2 (and D_2, T_2), which will be the subject of future work. The ultimate way, however, is the direct nonadiabatic calculation currently being pursued by Komasa [26]. In addition, our results can be extended to heteronuclear molecules (such as HD) without major modifications. Moreover, we note that an analogous method can be used to derive formulas for nonadiabatic corrections for the electric polarizability and QED corrections to transition energies.

Acknowledgements

We acknowledge interesting discussions with F. Merkt.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

M.S. acknowledges support from the National Science Center (Poland) Grant No. 2019/34/E/ST4/00451.

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Appendix A. Alternative Calculation of Q_2

$Q_2(R)$ requires evaluation of $\langle\nabla^k_R\phi_{\Sigma^+}|\nabla^k_R\phi_{\rm el}\rangle$. Below we derive an explicit expression for Eq. (77), starting from Eq. (75),

$$\langle\nabla^k_R\phi_{\Sigma^+}|\nabla^k_R\phi_{\rm el}\rangle = \frac{1}{2}\,\frac{d}{d\,\xi}\bigg|_{\xi=0}\,[\vec{v}^T\,\mathcal{B}\,\vec{v}+(\partial_R\vec{v})^T\,\mathcal{N}\,\partial_R\vec{v}+2\,(\partial_R\vec{v})^T\,\mathcal{A}\,\vec{v}]_\xi\,. \tag{A1}$$

The matrices $\mathcal{B},\mathcal{N},\mathcal{A}$ do not depend on δH, so

$$\langle\nabla^k_R\phi_{\Sigma^+}|\nabla^k_R\phi_{\rm el}\rangle = \vec{v}^T\,\mathcal{B}\,\delta\vec{v}+(\partial_R\vec{v})^T\,\mathcal{N}\,\partial_R\delta\vec{v}+(\partial_R\delta\vec{v})^T\,\mathcal{A}\,\vec{v}+(\partial_R\vec{v})^T\,\mathcal{A}\,\delta\vec{v}\,, \tag{A2}$$

where

$$\delta\vec{v} = \frac{d\vec{v}}{d\xi}\bigg|_{\xi=0}\,. \tag{A3}$$

$\delta\vec{v}$ can be obtained by differentiation of the linear equation $(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\vec{v}=0$ over ξ

$$(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\delta\vec{v}+(\delta\mathcal{H}-\delta\mathcal{E}_{\rm el}\,\mathcal{N})\vec{v}=0\,, \tag{A4}$$

and by differentiation of the normalization condition $(\vec{v}^T\mathcal{N}\vec{v})_\xi=1$ over ξ, so $\delta\vec{v}$ is orthogonal to $\vec{v}$, namely $\vec{v}^T\mathcal{N}\delta\vec{v}=0$, and

$$\delta\vec{v} = \frac{1}{(\mathcal{E}_{\rm el}\,\mathcal{N}-\mathcal{H})'}\,\delta\mathcal{H}\,\vec{v}\,, \tag{A5}$$

where $\delta\mathcal{H}_{kl}\equiv\big\langle\psi_k\big|\delta H\big|\psi_l\big\rangle$. Next, we differentiate Eq. (71) over ξ

$$(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\,\partial_R\delta\vec{v}+(\delta\mathcal{H}-\delta\mathcal{E}_{\rm el}\,\mathcal{N})\,\partial_R\vec{v}+\partial_R(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\,\delta\vec{v}+\partial_R\,(\delta\mathcal{H}-\delta\mathcal{E}_{\rm el}\,\mathcal{N})\,\vec{v}=0\,, \tag{A6}$$

to obtain

$$\begin{aligned}\partial_R\delta\vec{v} = {}& \frac{1}{(\mathcal{E}_{\rm el}\,\mathcal{N}-\mathcal{H})'}\,\big[\partial_R\,(\delta\mathcal{H}-\delta\mathcal{E}_{\rm el}\,\mathcal{N})\,\vec{v}+(\delta\mathcal{H}-\delta\mathcal{E}_{\rm el}\,\mathcal{N})\,\partial_R\vec{v}+\partial_R(\mathcal{H}-\mathcal{E}_{\rm el}\,\mathcal{N})\,\delta\vec{v}\big]\\ & -\vec{v}\,\big[(\partial_R\vec{v})^T\,\mathcal{N}\,\delta\vec{v}+\vec{v}^T\,\partial_R\mathcal{N}\,\delta\vec{v}\big]\,,\end{aligned} \tag{A7}$$

where the last term (parallel to $\vec{v}$) is found by differentiation of Eq. (74)

$$2\,(\partial_R\vec{v})^T\,\mathcal{N}\,\vec{v}+\vec{v}^T\,\partial_R\mathcal{N}\,\vec{v}=0\,, \tag{A8}$$

over ξ

$$(\partial_R\delta\vec{v})^T\,\mathcal{N}\,\vec{v}+(\partial_R\vec{v})^T\,\mathcal{N}\,\delta\vec{v}+\vec{v}^T\,\partial_R\mathcal{N}\,\delta\vec{v}=0\,. \tag{A9}$$

The derivative of $\mathcal{E}_{\rm el}$ over R is obtained from

$$0 = \partial_R[\vec{v}^T(\mathcal{H} - \mathcal{E}_{\rm el}\,\mathcal{N})\vec{v}] = \vec{v}^T(\partial_R\mathcal{H} - \partial_R\mathcal{E}_{\rm el}\,\mathcal{N} - \mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\vec{v}\,, \tag{A10}$$

so

$$\partial_R\mathcal{E}_{\rm el} = \vec{v}^T(\partial_R\mathcal{H} - \mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\vec{v} \tag{A11}$$

Similarly, the derivative of $\delta\mathcal{E}_{\rm el} = \vec{v}^T\delta\mathcal{H}\vec{v}$ over R is obtained from

$$\partial_R(\mathcal{E}_{\rm el} + \delta\mathcal{E}_{\rm el}) = (\vec{v}^T + \delta\vec{v}^T)(\partial_R\mathcal{H} + \partial_R\delta\mathcal{H} - (\mathcal{E}_{\rm el} + \delta\mathcal{E}_{\rm el})\,\partial_R\mathcal{N})(\vec{v} + \delta\vec{v}) \tag{A12}$$

so

$$\partial_R\delta\mathcal{E}_{\rm el} = \vec{v}^T(\partial_R\delta\mathcal{H} - \delta\mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\vec{v} + 2\,\vec{v}^T(\partial_R\mathcal{H} - \mathcal{E}_{\rm el}\,\partial_R\mathcal{N})\delta\vec{v} \tag{A13}$$

Summarizing, one calculates Q_2 using Eq. (A2), with $\vec{v}$ obtained from Eq. (69), $\partial_R\vec{v}$ from Eq. (72), $\delta\vec{v}$ from Eq. (A5), $\partial_R\delta\vec{v}$ from Eq. (A7), $\partial_R\mathcal{E}_{\rm el}$ from (A11), and with $\partial_R\delta\mathcal{E}_{\rm el}$ from (A13).

Table A1. Numerical results for $D^{(0)}(R) = \frac{3}{2}Q_0(R)$ and $D^{(1)}(R) = \frac{3}{2}\sum_{i=1\ldots 4} Q_i(R)$. For $R < 10$ au we used the single-sector JC basis ($y = x = 0, \alpha = u = w$, $\Omega = 15, 16$), and for $R \geq 10$ au a single-sector HL basis ($\alpha = -y = x = u = w = 1/2$, $\Omega = 13, 14$).

R	$D^{(0)}(R)$	$D^{(1)}(R)$	R	$D^{(0)}(R)$	$D^{(1)}(R)$
0.1	−0.002 951 435(4)	−0.006 320(8)	4.6	−0.424 390 384 5(3)	−1.467 309 361 8(6)
0.2	−0.011 709 44(1)	−0.021 260(9)	4.8	−0.350 786 848 4(3)	−1.188 240 220 9(5)
0.3	−0.026 051 81(1)	−0.042 022(2)	5	−0.286 972 211 6(3)	−0.953 297 753 5(4)
0.35	−0.035 231 298(6)	−0.054 283 8(9)	5.2	−0.232 780 011 8(3)	−0.759 883 733 8(4)
0.4	−0.045 699 563(4)	−0.067 746 1(4)	5.4	−0.187 509 569 7(3)	−0.602 961 001 4(4)
0.45	−0.057 417 112(3)	−0.082 401 4(2)	5.6	−0.150 184 321 3(3)	−0.476 861 125 0(4)
0.5	−0.070 343 172(2)	−0.098 257 1(1)	5.8	−0.119 731 937 2(3)	−0.376 191 601 6(4)
0.55	−0.084 435 808(2)	−0.115 330 71(8)	6	−0.095 097 737 3(2)	−0.296 203 401 3(4)
0.6	−0.099 651 980(2)	−0.133 646 81(6)	6.5	−0.052 855 949 0(1)	−0.162 042 133 8(2)
0.65	−0.115 947 571(2)	−0.153 234 91(5)	7	−0.029 133 976 98(9)	−0.088 399 260 3(1)
0.7	−0.133 277 395(1)	−0.174 128 40(4)	7.5	−0.016 075 011 17(5)	−0.048 441 307 7(4)
0.75	−0.151 595 187(1)	−0.196 363 74(3)	8	−0.008 963 605 49(3)	−0.026 898 288 7(7)
0.8	−0.170 853 579 1(9)	−0.219 979 96(2)	8.5	−0.005 101 602 00(2)	−0.015 283 959(1)
0.85	−0.191 004 076 5(8)	−0.245 018 41(1)	9	−0.002 992 484 99(1)	−0.008 973 903(1)
0.9	−0.211 997 024 8(7)	−0.271 522 49(1)	9.5	−0.001 823 758 72(1)	−0.005 487 953 2(1)
0.95	−0.233 781 573 5(6)	−0.299 537 567(8)	10	−0.001 160 487 87(7)	−0.003 511 018 5(2)
1	−0.256 305 639 0(5)	−0.329 110 882(6)	10.5	−0.000 771 617 62(5)	−0.002 349 925 1(2)
1.05	−0.279 515 865 2(5)	−0.360 291 479(5)	11	−0.000 534 517 89(3)	−0.001 639 140 3(1)
1.1	−0.303 357 584 4(5)	−0.393 130 134(4)	11.5	−0.000 383 687 60(2)	−0.001 184 382 29(9)
1.15	−0.327 774 779 1(4)	−0.427 679 284(4)	12	−0.000 283 632 66(1)	−0.000 880 703 22(8)
1.2	−0.352 710 044 2(4)	−0.463 992 910(3)	12.5	−0.000 214 676 34(1)	−0.000 669 983 92(6)
1.25	−0.378 104 552 1(4)	−0.502 126 397(3)	13	−0.000 165 571 539(7)	−0.000 518 962 39(5)
1.3	−0.403 898 020 3(4)	−0.542 136 330(3)	13.5	−0.000 129 649 273(5)	−0.000 407 848 30(4)
1.32	−0.414 313 331 5(4)	−0.558 678 568(3)	14	−0.000 102 794 279(3)	−0.000 324 366 36(3)
1.34	−0.424 778 590 6(4)	−0.575 533 947(3)	14.5	−0.000 082 364 189(2)	−0.000 260 585 51(2)
1.36	−0.435 289 738 8(4)	−0.592 706 189(3)	15	−0.000 066 598 895(2)	−0.000 211 187 81(1)
1.38	−0.445 842 678 0(4)	−0.610 199 025(2)	15.5	−0.000 054 287 879(1)	−0.000 172 492 27(1)
1.39	−0.451 133 528 1(4)	−0.619 066 831(2)	16	−0.000 044 576 061 9(6)	−0.000 141 883 297(9)
1.4	−0.456 433 271 5(4)	−0.628 016 185(2)	16.5	−0.000 036 846 108 9(4)	−0.000 117 462 538(8)
1.401 1	−0.457 016 763 8(4)	−0.629 005 612(2)	17	−0.000 030 644 336 2(2)	−0.000 097 828 413(8)
1.41	−0.461 741 385 1(4)	−0.637 047 552(2)	17.5	−0.000 025 632 422 9(1)	−0.000 081 931 504(7)
1.42	−0.467 057 343 2(4)	−0.646 161 396(2)	18	−0.000 021 554 967 77(8)	−0.000 068 976 789(6)
1.44	−0.477 710 677 7(4)	−0.664 638 373(2)	18.5	−0.000 018 217 128 59(4)	−0.000 058 355 868(6)
1.46	−0.488 389 020 5(4)	−0.683 450 812(2)	19	−0.000 015 468 883 22(2)	−0.000 049 598 999(6)
1.48	−0.499 088 077 7(4)	−0.702 602 387(2)	19.5	−0.000 013 193 758 12(1)	−0.000 042 340 584(5)
1.5	−0.509 803 516 5(4)	−0.722 096 737(2)	20	−0.000 011 300 639 904(7)	−0.000 036 293 994(5)
1.55	−0.536 634 995 1(4)	−0.772 355 724(2)	21	−0.000 008 388 192 347(2)	−0.000 026 977 838(5)
1.6	−0.563 472 053 5(4)	−0.824 833 971(2)	22	−0.000 006 316 417 375 6(5)	−0.000 020 338 922(4)
1.65	−0.590 243 824 8(4)	−0.879 582 963(2)	23	−0.000 004 818 654 241 7(2)	−0.000 015 532 065(3)
1.7	−0.616 877 988 5(4)	−0.936 649 816(2)	24	−0.000 003 719 879 686 32(7)	−0.000 012 001 058(3)
1.8	−0.669 437 307 5(4)	−1.057 894 508(2)	25	−0.000 002 902 964 190 07(5)	−0.000 009 372 825(2)
1.9	−0.720 545 075 7(4)	−1.188 794 210(2)	26	−0.000 002 288 127 320 35(3)	−0.000 007 392 753(2)
2	−0.769 579 093 0(4)	−1.329 381 366(2)	27	−0.000 001 820 146 001 64(3)	−0.000 005 884 301(2)
2.1	−0.815 905 362 7(4)	−1.479 406 343(2)	28	−0.000 001 460 226 595 03(2)	−0.000 004 723 262(1)
2.2	−0.858 885 741 2(4)	−1.638 231 196(2)	29	−0.000 001 180 743 679 13(2)	−0.000 003 821 075(1)
2.3	−0.897 888 100 1(3)	−1.804 709 949(2)	30	−0.000 000 961 775 941 64(1)	−0.000 003 113 796(1)
2.4	−0.932 299 240 0(3)	−1.977 064 939(2)	31	−0.000 000 788 789 220 76(4)	−0.000 002 554 730(2)
2.5	−0.961 540 620 6(3)	−2.152 775 178(2)	32	−0.000 000 651 064 123 09(3)	−0.000 002 109 401(2)
2.6	−0.985 086 710 8(3)	−2.328 499 368(2)	33	−0.000 000 540 614 443 29(3)	−0.000 001 752 106(2)
2.7	−1.002 485 402 7(3)	−2.500 061 558(2)	34	−0.000 000 451 433 779 64(2)	−0.000 001 463 496(2)
2.8	−1.013 379 503 2(3)	−2.662 528 726(2)	35	−0.000 000 378 964 564 88(2)	−0.000 001 228 881(1)
2.9	−1.017 527 860 2(2)	−2.810 404 164(2)	36	−0.000 000 319 719 719 55(2)	−0.000 001 037 014(1)
3	−1.014 824 274 6(2)	−2.937 946 270(2)	37	−0.000 000 271 010 266 92(1)	−0.000 000 879 217(1)
3.1	−1.005 312 098 0(2)	−3.039 599 290(2)	38	−0.000 000 230 747 325 92(1)	−0.000 000 748 746(1)
3.2	−0.989 192 424 6(1)	−3.110 494 365(2)	39	−0.000 000 197 296 853 86(1)	−0.000 000 640 322(1)
3.3	−0.966 824 133 6(1)	−3.146 952 952(2)	40	−0.000 000 169 372 165 56(1)	−0.000 000 549 788(1)
3.4	−0.938 714 739 4(1)	−3.146 909 544(1)	41	−0.000 000 145 953 755 17(3)	−0.000 000 473 846(2)
3.5	−0.905 502 003 6(1)	−3.110 174 370(1)	42	−0.000 000 126 229 022 94(2)	−0.000 000 409 869(2)
3.6	−0.867 927 383 9(1)	−3.038 481 851(1)	43	−0.000 000 109 546 633 34(2)	−0.000 000 355 749(2)
3.7	−0.826 803 440 0(1)	−2.935 311 834(1)	44	−0.000 000 095 381 712 57(2)	−0.000 000 309 788(2)
3.8	−0.782 978 067 0(1)	−2.805 516 542(1)	45	−0.000 000 083 309 135 50(2)	−0.000 000 270 610(2)
3.9	−0.737 298 724 5(1)	−2.654 822 813(1)	46	−0.000 000 072 982 892 96(1)	−0.000 000 237 094(2)
4	−0.690 579 643 5(2)	−2.489 296 550(1)	47	−0.000 000 064 120 059 59(1)	−0.000 000 208 324(2)
4.2	−0.596 955 200 4(2)	−2.136 860 879 3(9)	48	−0.000 000 056 488 265 29(1)	−0.000 000 183 546(1)
4.4	−0.507 085 534 9(3)	−1.787 644 342 5(7)	50	−0.000 000 044 184 093 148(8)	−0.000 000 143 591(1)

Table A2. Transition rates for the Q ($J'' = J'$), S ($J'' = J' - 2$), and O ($J'' = J' + 2$) branches of the fundamental ($\nu = 1 \to 0$) band of H_2 in units of 10^{-8} s^{-1}. A_{M1} is the magnetic dipole transition rate with the uncertainty due to unknown finite-nuclear-mass corrections estimated as $\sim 2\frac{m_e}{m_n} A_{M1}$. δA^X_{E2} is the difference in the E2 transition rate between those calculated with the mass-corrected quadrupole operator ($D^{(1)}$) with the adiabatically corrected nuclear wavefunction with $X = Q, S, O$, for Q-, S-, and O-branch, respectively; and the E2 rate in the BO approximation ($D^{(0)}$ operator and BO nuclear wavefunction). The E2 rates' uncertainty is now dominated by the unknown relativistic corrections, estimated by $\sim \alpha^2 A_{E2} \approx 0.5 \cdot 10^{-4} A_{E2}$. Physical constants are from Ref. [22].

J'	A_{M1}	A^Q_{E2}	$10^2 \cdot \delta A^Q_{E2}/A^Q_{E2}$	A^S_{E2}	$10^2 \cdot \delta A^S_{E2}/A^S_{E2}$	A^O_{E2}	$10^2 \cdot \delta A^O_{E2}/A^O_{E2}$
0	0.0	0.0	–	0.0	–	85.601 2	0.43
1	0.071 263	43.018 58	0.44	0.0	–	42.355 57	0.43
2	0.213 856	30.394 75	0.44	25.345 57	0.45	29.048 50	0.42
3	0.427 900	27.907 32	0.44	34.821 58	0.47	20.885 10	0.42
4	0.713 535	26.592 35	0.44	39.957 98	0.48	15.022 87	0.42
5	1.070 888	25.537 08	0.45	42.228 16	0.50	10.645 77	0.41
6	1.500 002	24.520 37	0.45	42.056 38	0.52	7.379 740	0.41
7	2.000 858	23.471 48	0.45	39.717 09	0.55	4.983 036	0.41
8	2.573 176	22.367 33	0.46	35.542 90	0.59	3.266 392	0.41
9	3.216 497	21.203 88	0.46	29.974 95	0.64	2.071 560	0.41
10	3.930 060	19.985 88	0.47	23.555 94	0.71	1.266 124	0.41
11	4.712 747	18.722 64	0.47	16.897 15	0.82	0.742 0804	0.41
12	5.563 033	17.425 88	0.48	10.634 77	1.00	0.414 3583	0.41
13	6.478 907	16.108 52	0.49	5.384 776	1.34	0.218 4628	0.42
14	7.457 797	14.783 94	0.50	1.702 894	2.26	0.107 4067	0.42
15	8.496 474	13.465 42	0.51	0.053 1505	11.79	0.048 3604	0.42
16	9.590 935	12.165 80	0.52	0.786 6411	−2.98	0.019 4046	0.42
17	10.736 26	10.897 15	0.53	4.130 413	−1.21	0.006 6420	0.43
18	11.926 43	9.670 58	0.55	10.185 26	−0.71	0.001 7974	0.43
19	13.154 12	8.496 08	0.56	18.930 57	−0.48	0.000 3309	0.43
20	14.410 37	7.382 42	0.58	30.234 23	−0.35	0.000 0286	0.44
21	15.684 30	6.337 12	0.60	43.865 42	−0.27	0.000 000 270	0.44
22	16.962 60	5.366 34	0.63	59.508 71	−0.21		
23	18.228 98	4.474 97	0.66	76.777 73	−0.17		
24	19.463 51	3.666 56	0.69	95.227 4	−0.14		
25	20.641 62	2.943 40	0.73	114.363 4	−0.12		
26	21.732 96	2.306 50	0.78	133.648 6	−0.11		
27	22.699 75	1.755 61	0.84	152.503 8	−0.10		
28	23.494 67	1.289 29	0.92	170.303 9	−0.09		
29	24.057 79	0.904 82	1.01	186.363 0	−0.09		
30	24.311 98	0.598 28	1.14	199.905 3	−0.08		

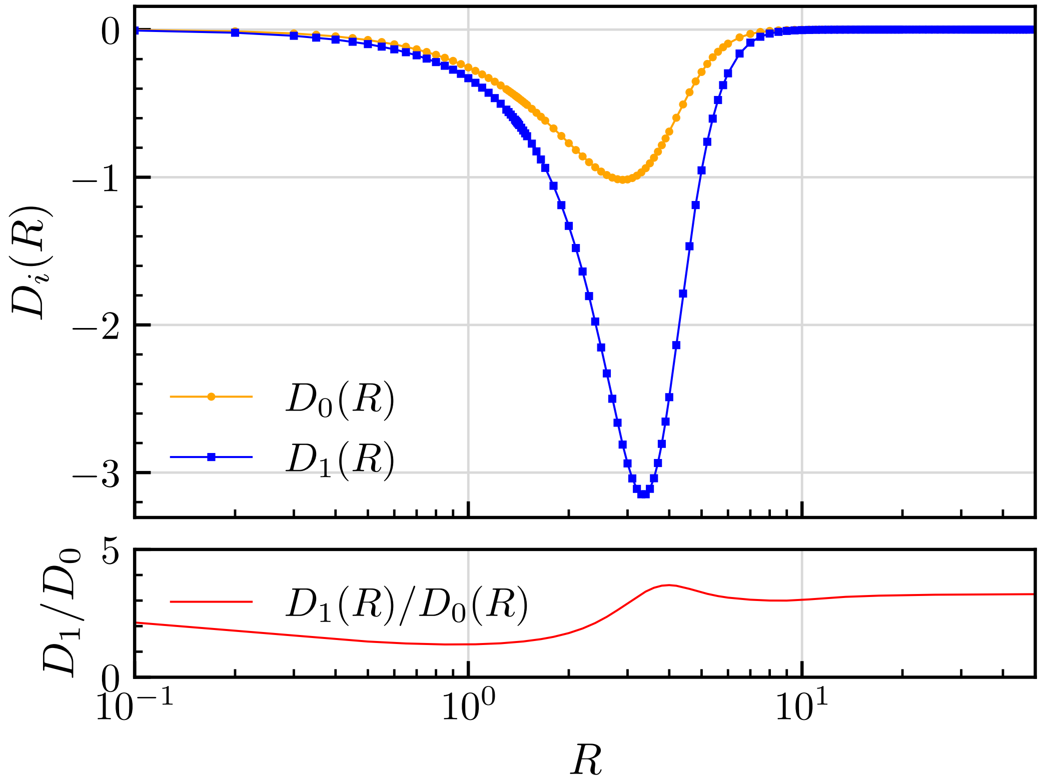

Figure A1. Top: Born-Oppenheimer approximated quadrupole operator $D^{(0)}(R)$ (orange; circles) and its leading-order mass correction $D^{(1)}(R)$ (blue; squares). Bottom: Their ratio, supporting the claim that their leading-order long-range asymptotics is the same ($\sim R^{-6}$) up to a constant relative factor of about 3.25(5).