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 the finite nuclear mass corrections to the Born-Oppenheimer approximation have to be accounted for. It is shown that they can be obtained systematically in the perturbative approach. 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 presented.

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I. INTRODUCTION

In the calculation of some molecular property, the magnetic shielding for example, one usually assumes fixed position of nuclei, the so called Born-Oppenheimer (BO) approximation and at the final stage, averages over the appropriate vibration-rotational function. The principal question we address in this work is, what are the finite nuclear mass corrections to various physical properties such as relativistic energies, polarizabilities or the mentioned magnetic shielding evaluated in the BO approximation. The 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 \(\text{H}_2\text{O}\), or to the evaluation of the nuclear spin-rotation and shielding constants. In this work we demonstrate the applicability of the nonadiabatic perturbation theory \([3]\) 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, 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 \(\text{H}_2\) \([4, 5]\), the transition electric-dipole moment of LiH \([6]\), or in the shielding constant of \(\text{H}_2\) 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 function. We do not consider here the second order corrections in the nuclear Hamiltonian \(H_n\), but for consistency regard them also as the nonadiabatic corrections, although of higher order.

In Sec. II we define the reference frame and split the nonrelativistic Hamiltonian into the electronic and nuclear parts. In Sec. III we briefly present nonadiabatic perturbation theory on the basis of Ref. \([3]\), include nonadiabatic corrections to the BO wave function and derive general formulae for the 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. Other examples, the finite nuclear mass corrections to electric properties of molecules are derived in Sec. V, and to magnetic properties in Sec. VI. Finally, the obtained results are briefly summarized in Sec. VII.

II. NONRELATIVISTIC HAMILTONIAN

We consider a neutral diatomic molecule with the Hamiltonian

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

(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

\[ \vec{R}_A = \vec{R}_G + \epsilon_B \vec{R}, \]  

(2)

\[ \vec{R}_B = \vec{R}_G - \epsilon_A \vec{R}, \]  

(3)

\[ \vec{x}_a = \vec{R}_G + \vec{x}_a, \]  

(4)

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

\[ \vec{p}_A = \epsilon_A \vec{P}_G + \vec{P} - \epsilon_A \sum_a \vec{q}_a, \]  

(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)

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

\[ H = \sum_a \frac{\vec{q}_a^2}{2m} + V + \left( \frac{1}{2m_A} + \frac{1}{2m_B} \right) \vec{P}^2 + \left( \frac{\epsilon_A^2}{2m_A} + \frac{\epsilon_B^2}{2m_B} \right) \left( \sum_a \vec{q}_a \right)^2 - \left( \frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B} \right) \vec{P} \cdot \sum_a \vec{q}_a. \]  

(8)
The last term in the above is transformed by the unitary transformation

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

(9)

where

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

(10)

and

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

(11)

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

$$\tilde{H} = H_{el} + H_n,$$

(12)

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

(13)

$$H_n = \left( \frac{1}{2m_A} + \frac{1}{2m_B} \right) \vec{P}^2 + \left( \frac{\epsilon_A^2}{2m_A} + \frac{\epsilon_B^2}{2m_B} \right) \left( \sum_a \vec{q}_a \right)^2$$

$$-m \left( \frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B} \right) \sum_a \vec{x}_a \cdot \nabla_R(V)$$

$$= H'_n + H''_n,$$

(14)

(15)

where $H'_n$ includes the first term and $H''_n$ 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 the vanishing total momentum is defined by

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

(16)

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

$$\vec{J} = \sum_a \vec{x}_a \times \vec{q}_a + \vec{R} \times \vec{P} \equiv \vec{J}_{el} + \vec{J}_n$$

(17)

is split into electronic $\vec{J}_{el}$ and nuclear $\vec{J}_n$ parts, and this $\vec{J}$ is not being modified by the unitary transformation of Eq. (10).
III. NONADIABATIC PERTURBATION THEORY

The total nonrelativistic wave function $\phi$ of an arbitrary molecule is the solution of the stationary Schrödinger equation

$$[H - E] |\phi\rangle = 0,$$

(18)

with the Hamiltonian $H$ being a sum of the electronic $H_{\text{el}}$ and nuclear $H_{\text{n}}$ parts, Eq. (12).

In the adiabatic approximation $\phi = \phi_a$, where

$$\phi_a(\vec{x}, \vec{R}) = \phi_{\text{el}}(\vec{x}) \chi(\vec{R})$$

(19)

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

$$[H_{\text{el}} - E_{\text{el}}(\vec{R})] |\phi_{\text{el}}\rangle = 0,$$

(20)

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

$$[H_{\text{n}} + E_a(\vec{R}) + E_{\text{el}}(\vec{R}) - E_a] |\chi\rangle = 0,$$

(21)

where

$$E_a(\vec{R}) = \langle \phi_{\text{el}} | H_{\text{n}} | \phi_{\text{el}} \rangle_{\text{el}}.$$  

(22)

In the nonadiabatic perturbation theory, the total wave function

$$\phi = \phi_a + \delta\phi_{\text{na}} = \phi_{\text{el}} \chi + \delta\phi_{\text{na}}$$

(23)

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

$$\delta\phi_{\text{na}} = \phi_{\text{el}} \delta\chi + \delta'\phi_{\text{na}},$$

(24)

obeying the following orthogonality conditions

$$\langle \delta'\phi_{\text{na}} | \phi_{\text{el}} \rangle_{\text{el}} = 0,$$

(25)

$$\langle \delta\chi | \chi \rangle = 0,$$

(26)
which imply the normalization condition \( \langle \phi_a | \phi \rangle = 1 \).

In the first order in \( H_n \) of the nonadiabatic perturbation theory one has

\[
|\delta' \phi_{na}^{(1)}\rangle = \frac{1}{(E_{el} - H_{el})'} H_n |\phi_{el} \rangle, \tag{27}
\]

and in the second order

\[
|\delta' \phi_{na}^{(2)}\rangle = \frac{1}{(E_{el} - H_{el})'} (H_n + E_{el} - E_a) \frac{1}{(E_{el} - H_{el})'} H_n |\phi_{el} \rangle, \tag{28}
\]

where \( 1/(E_{el} - H_{el})' \) denotes resolvent with the reference state \( \phi_{el} \) 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 \( H_n \), and thus derivatives with respect to \( \vec{R} \). These derivatives can be calculated with the help of the following formulae

\[
\vec{\nabla}_R |\phi_{el} \rangle = \frac{1}{(E_{el} - H_{el})'} \vec{\nabla}_R (V)|\phi_{el} \rangle, \tag{29}
\]

\[
\vec{\nabla}_R \left[ \frac{1}{(E_{el} - H_{el})'} \right] = \frac{1}{(E_{el} - H_{el})'} \vec{\nabla}_R (V - E_{el}) \frac{1}{(E_{el} - H_{el})'} \bigg[ -\vec{\nabla}_R (V)|\phi_{el} \rangle \langle \phi_{el} | \\
-|\phi_{el} \rangle \langle \phi_{el} | \vec{\nabla}_R (V) \frac{1}{(E_{el} - H_{el})'^2} \bigg]. \tag{30}
\]

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 \( H_2 \) 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 \( \partial (V - E_{el})/\partial R \), namely

\[
\vec{\nabla}_R |\phi_{el} \rangle = \vec{n} \frac{1}{(E_{el} - H_{el})'} \frac{\partial V}{\partial R} |\phi_{el} \rangle - \frac{i}{R} \vec{n} \times \vec{J}_n |\phi_{el} \rangle. \tag{32}
\]

For example the adiabatic correction to energy becomes

\[
E_a(R) = \langle \phi_{el} | H_n |\phi_{el} \rangle = \langle \phi_{el} | H''_{na} + \frac{\vec{J}_n^2}{2 m_n R^2} |\phi_{el} \rangle + \langle \phi_{el} | \frac{\partial V}{\partial R} \frac{1}{(E_{el} - H_{el})'^2} \frac{\partial V}{\partial R} |\phi_{el} \rangle, \tag{33}
\]

where \( m_n \) is the nuclear reduced mass and for \( \Sigma \) electronic state \( \vec{J}_n |\phi_{el} \rangle \) can be replaced by \(-\vec{J}_{el} |\phi_{el} \rangle \). In this way one avoids summation over intermediate states with the \( \Pi \) symmetry.
A. First order matrix elements

We will use here this nonadiabatic perturbation theory to derive the finite nuclear mass corrections to various matrix elements in the general form. Later we will analyze specific examples. Consider 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

$$\langle Q \rangle^{(0)} \equiv \langle \phi_{el} \chi_f | Q | \phi_{el} \chi_i \rangle = \langle \chi_f | \langle Q \rangle^{(0)}_{el} | \chi_i \rangle,$$  

(34)

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

(35)

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

$$\langle Q \rangle^{(1)} = \langle \phi_{el} \chi_f | H_n \frac{1}{(\mathcal{E}_{el} - H_{el})'} Q | \phi_{el} \chi_i \rangle \langle \phi_{el} \chi_f \phi_{el} | \chi_i \rangle + \langle \phi_{el} \chi_f | Q \frac{1}{(\mathcal{E}_{el} - H_{el})'} H_n | \phi_{el} \chi_i \rangle.$$  

(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 the nonadiabatic perturbation theory

$$\langle Q \rangle^{(2)} = \langle \phi_{el} \chi_f | H_n \frac{1}{(\mathcal{E}_{el} - H_{el})'} (H_n + \mathcal{E}_{el} - E_a) \frac{1}{(\mathcal{E}_{el} - H_{el})'} Q | \phi_{el} \chi_i \rangle \langle \phi_{el} \chi_f \phi_{el} | \chi_i \rangle + \langle \phi_{el} \chi_f | Q \frac{1}{(\mathcal{E}_{el} - H_{el})'} (H_n + \mathcal{E}_{el} - E_a) \frac{1}{(\mathcal{E}_{el} - H_{el})'} H_n | \phi_{el} \chi_i \rangle \langle \phi_{el} \chi_f \phi_{el} | \chi_i \rangle + \langle \phi_{el} \chi_f | H_n \frac{1}{(\mathcal{E}_{el} - H_{el})'} (Q - \langle Q \rangle^{(0)}_{el}) \frac{1}{(\mathcal{E}_{el} - H_{el})'} H_n | \phi_{el} \chi_i \rangle.$$  

(37)

Additional corrections due to $\delta \chi$ in Eq. (27) can easily be included in the $\langle Q \rangle^{(0)}$ and $\langle Q \rangle^{(1)}$ by replacing $\chi$ 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)

$$\langle Q \rangle^{(1)} = \int d^3 R \left\{ (\chi_f^* \chi_i) \left[ \langle H_n \phi_{el} | \frac{1}{(\mathcal{E}_{el} - H_{el})'} Q | \phi_{el} \rangle + \langle \phi_{el} | Q \frac{1}{(\mathcal{E}_{el} - H_{el})'} | H_n \phi_{el} \rangle \right] - \frac{\nabla^2}{2m_n} \left[ \langle \nabla R \phi_{el} | \frac{1}{(\mathcal{E}_{el} - H_{el})'} Q | \phi_{el} \rangle + \langle \phi_{el} | Q \frac{1}{(\mathcal{E}_{el} - H_{el})'} | \nabla R \phi_{el} \rangle \right] \right\}$$  

(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

$$\langle Q \rangle^{(1)} = \langle \chi_t | Q_{el}^{(1)} | \chi_i \rangle,$$

$$\langle Q \rangle^{(1)}_{el} = \langle \phi_{el} | \nabla_n \frac{1}{(E_{el} - H_{el})} Q | \phi_{el} \rangle + \langle \phi_{el} | Q \phi_{el} | \nabla_n^{\prime} \frac{1}{(E_{el} - H_{el})} | \phi_{el} \rangle,$$

(39)

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

$$\langle \psi'_{el} | H_n | \psi_{el} \rangle = \langle \nabla R \psi'_{el} | \nabla R \psi_{el} \rangle / (2 m_n) + \langle \psi'_{el} | H''_{el} | \psi_{el} \rangle.$$

(41)

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

$$\langle Q \rangle^{(1)}_{el} = \frac{1}{2 m_n} \int \frac{d^3 R}{R^2} \left[ \langle J_i^n \chi_t \rangle^* \chi_i + \chi_i^* \langle J_i^n \chi_t \rangle \right] \times \left[ \langle \phi_{el} | Q_j^j \frac{1}{(E_{el} - H_{el})} J_j^n \phi_{el} \rangle + \langle J_j^n \phi_{el} | \overline{Q}^j \phi_{el} | \phi_{el} \rangle \right].$$

(42)

where $\overline{J}_n$ is defined in Eq. (17). Let us assume that $\phi_{el}$ is a $\Sigma$ state, then $\overline{J}_n | \phi_{el} \rangle = -\overline{J}_n | \phi_{el} \rangle$ and

$$\langle Q \rangle^{(1)}_{el} = -\langle \chi_t | \frac{J_i^n}{m_n R^2} \langle \phi_{el} | J_j^n \frac{1}{(E_{el} - H_{el})} Q_j^j | \phi_{el} \rangle \chi_i \rangle.$$  

(43)

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

**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 $\langle \phi_{el} | Q_1 | \phi_{el} \rangle = 0$ and introduce the notation

$$\langle Q_1 Q_2 \rangle \equiv \langle \phi | Q_1 \frac{1}{(E - H)^2} Q_2 | \phi \rangle + \text{c.c.}$$

(44)

In the leading order of the nonadiabatic perturbation theory this matrix element is

$$\langle Q_1 Q_2 \rangle^{(0)} = \langle \chi | \langle Q_1 Q_2 \rangle^{(0)} | \chi \rangle,$$

$$\langle Q_1 Q_2 \rangle_{el}^{(0)} = \langle \phi_{el} | Q_1 \frac{1}{(E_{el} - H_{el})} Q_2 | \phi_{el} \rangle + \text{c.c.},$$

(45)

(46)
and the nonadiabatic correction is

\[ \langle Q_1 Q_2 \rangle^{(1)} = \langle \phi_{el} | Q_1 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} (H_n + \mathcal{E}_{el} - E_a) \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_2 | \phi_{el} \rangle \\
+ \langle \phi_{el} | H_n \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_1 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_2 | \phi_{el} \rangle \\
+ \langle \phi_{el} | Q_1 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_2 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} H_n | \phi_{el} \rangle + \text{c.c.} \] (47)

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

\[ \langle Q_1 Q_2 \rangle^{(1)} = \langle \chi | \langle Q_1 Q_2 \rangle_{el}^{(1)} | \chi \rangle \] (48)

\[ \langle Q_1 Q_2 \rangle_{el}^{(1)} = \langle \phi_{el} | Q_1 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} (\mathcal{H}_n - \mathcal{E}_a) \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_2 | \phi_{el} \rangle \\
+ \langle \phi_{el} | \mathcal{H}_n \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_1 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_2 | \phi_{el} \rangle \\
+ \langle \phi_{el} | Q_1 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} Q_2 \frac{1}{(\mathcal{E}_{el} - \mathcal{E}_{el})'} \mathcal{H}_n | \phi_{el} \rangle + \text{c.c.} \] (49)

These formulae will be used in the calculations of the nonadiabatic corrections to the shielding constant. The more general case with \( \langle \phi_{el} | Q_i | \phi_{el} \rangle \neq 0 \) 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 \( \delta Q \) with respect to \( Q \) of the nuclear Schrödinger equation, which includes the diagonal adiabatic correction \( \mathcal{E}_a \) in Eq. \( (21) \)

\[ \delta Q [H_n + \mathcal{E}_a(R) + \mathcal{E}_{el}(R) - E_a] | \chi \rangle = 0 , \] (50)

that is

\[ [H_n + \mathcal{E}_a(R) + \mathcal{E}_{el}(R) - E_a] | \delta Q \chi \rangle + [\delta Q \mathcal{E}_a(R) + \delta Q \mathcal{E}_{el}(R) - \delta Q E_a] | \chi \rangle = 0 . \] (51)

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

\[ \langle \phi | Q | \phi \rangle = \delta Q E \approx \delta Q E_a = \langle \chi | \delta Q \mathcal{E}_a(R) + \delta Q \mathcal{E}_{el}(R) | \chi \rangle . \] (52)
The perturbation of electronic energies \( \mathcal{E}_{\text{el}}(R) \) and \( \mathcal{E}_a(R) \) due to some operator \( Q \) can be obtained using the standard Rayleigh-Schrödinger perturbation theory and the result

\[
\langle \phi | Q | \phi \rangle = \langle \chi | \langle Q \rangle_{\text{el}}^{(0)} | \chi \rangle + \langle \chi | \langle Q \rangle_{\text{el}}^{(1)} | \chi \rangle + \ldots 
\]

(53)

which 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

\[
\delta_Q | \chi \rangle = \frac{1}{[E_a - H_n - \mathcal{E}_a(R) - \mathcal{E}_{\text{el}}(R)]'} \left[ \langle \phi_{\text{el}} | Q | \phi_{\text{el}} \rangle \right. \\
+ \langle \phi_{\text{el}} | H_n \frac{1}{(\mathcal{E}_{\text{el}} - \mathcal{E}_a)} Q | \phi_{\text{el}} \rangle + \langle \phi_{\text{el}} | Q \frac{1}{(\mathcal{E}_a - \mathcal{E}_{\text{el}})} H_n | \phi_{\text{el}} \rangle \left| \chi \right>. 
\]

(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 \( \delta_{Q_1 Q_2} \) of Eq. (21), and multiply from the left by \( \langle \chi | \)

\[
\langle \chi | \delta_{Q_1 Q_2} \mathcal{E}_a(R) + \delta_{Q_1 Q_2} \mathcal{E}_{\text{el}}(R) - \delta_{Q_1 Q_2} E_a | \chi \rangle + \langle \chi | \delta_{Q_1} \mathcal{E}_a(R) + \delta_{Q_1} \mathcal{E}_{\text{el}}(R) | \delta_{Q_2} \chi \rangle \\
+ \langle \chi | \delta_{Q_2} \mathcal{E}_a(R) + \delta_{Q_2} \mathcal{E}_{\text{el}}(R) | \delta_{Q_1} \chi \rangle = 0 . 
\]

(55)

This second order matrix element \( \langle Q_1 Q_2 \rangle \) is identified with \( \delta_{Q_1 Q_2} E_a \), and thus

\[
\langle Q_1 Q_2 \rangle = \langle \phi_1 | Q_1 \frac{1}{(E - H)'} Q_2 | \phi \rangle + \langle \phi_1 | Q_2 \frac{1}{(E - H)'} Q_1 | \phi \rangle \\
= \langle \chi | \delta_{Q_1 Q_2} \mathcal{E}_a(R) | \chi \rangle + \langle \chi | \delta_{Q_1} \mathcal{E}_a(R) | \delta_{Q_2} \chi \rangle + \langle \chi | \delta_{Q_2} \mathcal{E}_a(R) | \delta_{Q_1} \chi \rangle \\
+ \langle \chi | \delta_{Q_1 Q_2} \mathcal{E}_{\text{el}}(R) | \chi \rangle + \langle \chi | \delta_{Q_1} \mathcal{E}_{\text{el}}(R) | \delta_{Q_2} \chi \rangle + \langle \chi | \delta_{Q_2} \mathcal{E}_{\text{el}}(R) | \delta_{Q_1} \chi \rangle + \ldots \\
= \langle Q_1 Q_2 \rangle^{(0)} + \langle Q_1 Q_2 \rangle^{(1)} + \ldots ,
\]

(56)

where \( \delta_{Q_1 Q_2} \mathcal{E}_a \) and \( \delta_{Q_1 Q_2} \mathcal{E}_{\text{el}} \) are corrections to corresponding energies due to electronic operators \( Q_1 \) and \( Q_2 \), and

\[
\langle Q_1 Q_2 \rangle^{(0)} = \langle \chi | \langle \phi_{\text{el}} | Q_1 \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})'} Q_2 | \phi_{\text{el}} \rangle | \chi \rangle \\
+ \langle \chi | \langle Q_1 \rangle_{\text{el}}^{(0)} \frac{1}{[E_a - H_n - \mathcal{E}_a(R) - \mathcal{E}_{\text{el}}(R)]} \langle Q_2 \rangle_{\text{el}}^{(0)} | \chi \rangle + \text{c.c.} ,
\]

(57)
\[ \langle Q_1 Q_2 \rangle^{(1)} = \langle \phi_\text{el} | Q_1 \frac{1}{(E_\text{el} - H_\text{el})} \frac{\partial}{\partial \text{el}} - \mathcal{E}_\text{el} - \frac{1}{(E_\text{el} - H_\text{el})}' Q_2 | \phi_\text{el} \rangle | \chi \rangle \\
+ \langle \chi | \langle \phi_\text{el} | \frac{\partial}{\partial \text{el}} H_n \frac{1}{(E_\text{el} - H_\text{el})}' (Q_1 - \langle Q_1 \rangle^{(0)}_\text{el}) \frac{1}{(E_\text{el} - H_\text{el})}' Q_2 | \phi_\text{el} \rangle | \chi \rangle \\
+ \langle \chi | \langle \phi_\text{el} | Q_1 \frac{1}{(E_\text{el} - H_\text{el})}' (Q_2 - \langle Q_2 \rangle^{(0)}_\text{el}) \frac{1}{(E_\text{el} - H_\text{el})}' \frac{\partial}{\partial \text{el}} H_n | \phi_\text{el} \rangle | \chi \rangle \\
+ \langle \chi | \langle \phi_\text{el} | \frac{1}{[E_a - H_n - \mathcal{E}_\text{a}(R) - \mathcal{E}_\text{el}(R)]} \frac{\partial}{\partial \text{el}} Q_1^{(1)}_\text{el} \rangle | \chi \rangle \\
+ \langle \chi | \langle \phi_\text{el} | \frac{1}{[E_a - H_n - \mathcal{E}_\text{a}(R) - \mathcal{E}_\text{el}(R)]} Q_2^{(0)}_\text{el} \rangle | \chi \rangle + \text{c.c.} . \]  

(58)

In the case \( \langle Q_1 \rangle^{(0)}_\text{el} = \langle Q_2 \rangle^{(0)}_\text{el} = 0 \) above formulae coincide with those from 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 \( [\vec{P}^i , \vec{Q}^j] = 0 \), for example the electron-nucleus Breit interaction Eq. (65). Its matrix element between different rovibrational states is of the form

\[ \langle \phi_\text{el} \chi_f | Q | \phi_\text{el} \chi_i \rangle = \frac{i}{2} \langle \chi_f | \left( \langle \vec{\nabla}_R \phi_\text{el} | \vec{Q} \phi_\text{el} \rangle - \langle \phi_\text{el} | \vec{Q} \vec{\nabla}_R \phi_\text{el} \rangle \right) | \chi_i \rangle \\
+ \frac{i}{2} \left[ \langle \vec{\nabla}_R \chi_f | \langle \vec{Q} | \chi_i \rangle - \langle \chi_f | \langle \vec{Q} | \vec{\nabla}_R \chi_i \rangle \right]. \]  

(59)

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

\[ \langle \phi_\text{el} \chi_f | Q | \phi_\text{el} \chi_i \rangle = \langle \chi_f | \langle Q \rangle_\text{el} | \chi_i \rangle , \]  

(60)

\[ \langle Q \rangle_\text{el} = -i \langle \phi_\text{el} | \vec{Q} \vec{\nabla}_R \phi_\text{el} \rangle = i \langle \vec{\nabla}_R \phi_\text{el} | \vec{Q} \phi_\text{el} \rangle . \]  

(61)

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

\[ \langle \phi_\text{el} \chi_f | Q | \phi_\text{el} \chi_i \rangle = \langle \chi_f | \langle \vec{Q} \rangle_\text{el} \cdot \vec{P} | \chi_i \rangle = \langle \chi_f | \vec{P} \cdot \langle \vec{Q} \rangle_\text{el} | \chi_i \rangle . \]  

(62)

IV. RELATIVISTIC RECOIL CORRECTION TO ROVIBRATIONAL ENERGIES

This is the first and the simplest application of the nonadiabatic perturbation theory, 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 \[8, 9\]

$$
\delta H = \delta H_{el} + \delta H_n, \\
\delta H_{el} = \alpha^2 \left[ -\sum_a \frac{p_a^4}{8 m^2} + \sum_{a, X} \frac{Z_X \pi}{2 m^2} \delta^3(r_{aX}) + \sum_{a > b} \frac{\pi}{m^2} \delta^3(r_{ab}) - \sum_{a > b} \frac{1}{2 m^2} p_a^i \left( \frac{\delta_{ij}}{r_{ab}} + \frac{r_{ia} r_{ja}}{r_{ab}^3} \right) p_b^j \right] \\
\delta H_n = \alpha^2 \sum_{a, X} \frac{Z_X}{2 m m_X} p_a^i \left( \frac{\delta_{ij}}{r_{aX}} + \frac{r_{ia} r_{ja}}{r_{aX}^3} \right) p_X^j.
$$

The relativistic correction $E_{rel}$ to the energy, taking into account the transformation in Eq. \[10\], is

$$
E_{rel} = \langle \phi | \delta H | \phi \rangle = \langle \chi | (\delta H)_{el}^{(0)} | \chi \rangle + \langle \chi | (\delta H)_{el}^{(1)} | \chi \rangle + O(m/M)^{3/2};
$$

where

$$
\langle \delta H \rangle_{el}^{(0)} = \langle \phi_{el} | \delta H_{el} | \phi_{el} \rangle = \langle \delta H_{el} \rangle_{el},
$$

$$
\langle \delta H \rangle_{el}^{(1)} = \langle \phi_{el} | \delta H_n | \phi_{el} \rangle - m \left( \frac{\varepsilon_A}{m_A} - \frac{\varepsilon_B}{m_B} \right) \left( \phi_{el} | \sum_a \vec{x}_a \cdot \vec{\nabla}_R, \delta H_{el} | \phi_{el} \right) \\
+ 2 \langle \phi_{el} | \delta H_n \frac{1}{(E_{el} - H_{el})'} \vec{R} | \phi_{el} \rangle.
$$

As it have already been noticed in \[5\], relativistic recoil effects are of order $O(m/M)$ and can be expressed as a correction $\langle \delta H \rangle_{el}^{(1)}$ to the BO energy $E_{el}(R)$.

Since the wave function $\phi$ does not depend on $\vec{R}_G$, the momentum $\vec{P}_G$ implicitly present in $\delta H_n$ can be set to 0. Moreover, we chose $\vec{R}_G$ in dependence on the particular operator in $\delta H_{el}$, in such a way that the result of the transformation $\phi$ in Eq. \[10\], namely the second term in Eq. \[69\] vanishes. For example for the first, third and fourth term in $\delta H_{el}$ $\vec{R}_G$ 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 $\delta H_n$ in the geometrical center ($\varepsilon_A = \varepsilon_B = 1/2$). In this particular choice of $\vec{R}_G$, the derivative $\partial \delta H_{el} / \partial R$ that comes from $H_{el}''$ in Eq. \[69\] also vanishes and the relativistic finite nuclear mass correction can be rewritten to the form

$$
\langle \delta H \rangle_{el}^{(1)} = \langle \phi_{el} | \delta H_n | \phi_{el} \rangle + 2 \langle \phi_{el} | \delta H_{el} \frac{1}{(E_{el} - H_{el})'} \left( H_{el}'' + \frac{\vec{P}_{el}^2}{2 m_n R^2} \right) | \phi_{el} \rangle \\
+ \frac{1}{m_n} \langle \phi_{el} | \frac{\partial V}{\partial R} \frac{1}{(E_{el} - H_{el})'} \left( \delta H_{el} - \langle \delta H_{el} \rangle_{el} \right) \frac{1}{(E_{el} - H_{el})' \partial R} | \phi_{el} \rangle \\
+ \frac{1}{m_n} \langle \phi_{el} | \delta H_{el} \frac{1}{(E_{el} - H_{el})'} \left( \frac{\partial (V - E_{el})}{\partial R} \frac{1}{(E_{el} - H_{el})' \partial R} \right) | \phi_{el} \rangle.
$$
The expectation value of $\delta H_n$ is calculated according to Eq. (32), namely if

$$\delta H_n = \vec{Q}_1 \cdot \vec{\nabla}_R + Q_2,$$

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

$$\langle \phi_{el} | \delta H_n | \phi_{el} \rangle = \langle \phi_{el} | Q_2 | \phi_{el} \rangle + \langle \phi_{el} | \vec{n} \cdot \vec{Q}_1 \frac{1}{(E_{el} - H_{el})'} \frac{\partial V}{\partial R} | \phi_{el} \rangle + \frac{i}{R} \langle \phi_{el} | \vec{n} \times \vec{Q}_1 \cdot \vec{J}_n | \phi_{el} \rangle.$$ 

One may expect significant cancellations in the leading finite nuclear mass correction $\langle \delta H \rangle_{el}^{(1)}$ between the first and the second term 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. It is due to, for example, the second order in $H_n$ 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, 11, 12, 13], H$_2$ in [1], and LiH in [2]. There is a lot of literature on electric properties of molecules, in what we call 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 the homogenous electric field $\vec{E}$ is given by

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

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

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

and where $\vec{x}_A = e_B \vec{R}$ and $\vec{x}_B = -e_A \vec{R}$. We note that for charged molecular systems, the electric dipole moment has to be defined with respect to the mass center 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. (10). We will show below that 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 \( H_{\text{eff}} \) in the nuclear space

\[
H_{\text{eff}} = -\vec{D}_{\text{el}}(\vec{R}) \cdot \vec{E} - \frac{\alpha^{ij}_e(\vec{R})}{2} E^i E^j,
\]

(75)

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

\[
\vec{D}_n = \langle \chi_f | \vec{D}_{\text{el}} | \chi_i \rangle,
\]

(76)

and one notes that the matrix elements \( \vec{D}_n \) between the same nuclear states always vanish.

Similarly, the total electric dipole static polarizability is

\[
\alpha^{ij} = \langle \chi | \epsilon_{\text{el}}^{ij} | \chi \rangle - 2 \langle \chi | D^{i}_{\text{el}} \frac{1}{E_n - H - \mathcal{E}_a - \mathcal{E}_{\text{el}}} D^{j}_{\text{el}}^\dagger | \chi \rangle,
\]

(77)

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

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

\[
\vec{D}_{\text{el}} = \vec{D}^{(0)}_{\text{el}} + \vec{D}^{(1)}_{\text{el}},
\]

(78)

where

\[
\vec{D}^{(0)}_{\text{el}} = \langle \phi_{\text{el}} | \vec{D} | \phi_{\text{el}} \rangle,
\]

(79)

\[
\vec{D}^{(1)}_{\text{el}} = 2 \langle \phi_{\text{el}} | \vec{D} \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})} \vec{H}_n | \phi_{\text{el}} \rangle.
\]

(80)

For \( \Sigma \) electronic states the nonadiabatic correction can be rewritten to the form

\[
\vec{D}^{(1)}_{\text{el}} = 2 \langle \phi_{\text{el}} | \vec{D} \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})} \left( H''_n + \frac{\vec{J}^2_{\text{el}}}{2m_n R^2} \right) | \phi_{\text{el}} \rangle + \frac{i}{m_n R^2} \langle \phi_{\text{el}} | \vec{D} \times \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})} \vec{J}_{\text{el}} | \phi_{\text{el}} \rangle
\]

\[
+ \frac{1}{m_n} \langle \phi_{\text{el}} | \vec{D} \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})} \frac{\partial V - \mathcal{E}_{\text{el}}}{\partial R} \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})^2} \frac{\partial V}{\partial R} | \phi_{\text{el}} \rangle
\]

\[
+ \frac{1}{m_n} \langle \phi_{\text{el}} | \frac{\partial V}{\partial R} \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})} \left( \vec{D} - \vec{D}^{(0)}_{\text{el}} \right) \frac{1}{(\mathcal{E}_{\text{el}} - H_{\text{el}})^2} \frac{\partial V}{\partial R} | \phi_{\text{el}} \rangle.
\]

(81)
This result is in agreement with the previously obtained much simpler formula for the HD molecule \cite{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 $\vec{D}_n$ can be represented in terms of the matrix element of the electronic dipole moment $\vec{D}_{\text{el}}$ evaluated with nuclear functions $\chi_f^*$ and $\chi_i$, see Eq. (39). A similar result holds for the electric dipole static polarizability

$$\alpha_{\text{el}}^{ij} = \alpha_{\text{el}}^{(0)ij} + \alpha_{\text{el}}^{(1)ij},$$

where in the BO approximations it is

$$\alpha_{\text{el}}^{(0)ij} = -2 \langle \phi_{\text{el}} | D^i \frac{1}{(E_{\text{el}} - H_{\text{el}})'(E_{\text{el}} - H_{\text{el}})' - J_{\text{el}}} D^j | \phi_{\text{el}} \rangle,$$

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

$$\alpha_{\text{el}}^{(1)ij} = -2 \left[ \langle \phi_{\text{el}} | D^i \frac{1}{(E_{\text{el}} - H_{\text{el}})'(E_{\text{el}} - H_{\text{el}})' - J_{\text{el}}} D^j | \phi_{\text{el}} \rangle \right. \right.$$

$$+ \langle \phi_{\text{el}} | \vec{H}_{n} \frac{1}{(E_{\text{el}} - H_{\text{el}})'(E_{\text{el}} - H_{\text{el}})' - J_{\text{el}}} D^j | \phi_{\text{el}} \rangle$$

$$+ \langle \phi_{\text{el}} | D^i \frac{1}{(E_{\text{el}} - H_{\text{el}})'(E_{\text{el}} - H_{\text{el}})' - J_{\text{el}}} D^j | \phi_{\text{el}} \rangle \left. \right.$$

$$\left. + \langle \phi_{\text{el}} | \vec{H}_{n} \frac{1}{(E_{\text{el}} - H_{\text{el}})'(E_{\text{el}} - H_{\text{el}})' - J_{\text{el}}} D^j | \phi_{\text{el}} \rangle \right].$$

The explicit formula after taking the derivative with respect to $R$ is little bit too long to be written here, but can easily be obtained with the help of Eqs. (29,30,31). Eq. (77) in the adiabatic approximation, namely $\alpha_{\text{el}} \rightarrow \alpha_{\text{el}}^{(0)}$, $\vec{D}_{\text{el}} \rightarrow \vec{D}_{\text{el}}^{(0)}$ was already obtained in the literature [14, 15, 16]. Results for nonadiabatic corrections when $\alpha_{\text{el}} \rightarrow \alpha_{\text{el}}^{(1)}$, $\vec{D}_{\text{el}} \rightarrow \vec{D}_{\text{el}}^{(1)}$ 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 are reviewed in details by Flygare in \cite{18}. Here, we demonstrate that the nonadiabatic corrections can be implemented in the effective nuclear Hamiltonian, similarly to that in the BO approximation, namely

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

where it is understood that the electronic part of the angular momentum operator $\vec{J}_{\text{el}}$ Eq. (17) vanishes on $\chi$, $\eta$ 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, \( \sigma_{\text{el}} \) 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 interaction between nuclear magnetic moments, while the second term has not been investigated in the literature so far. Both terms will not be considered in this work. If two different nuclei are involved, each one has its own spin and magnetic moments, then 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 rotational magnetic moment \( \mu_J \) and spin rotation constant \( \eta \) and obtain nonadiabatic corrections to the shielding constant. These corrections, up 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 the homogenous magnetic field

\[
H_0 = \sum_{\beta} \frac{\hat{\pi}_\beta^2}{2 m_\beta} + V,
\]

(86)

where \( \beta \) enumerates 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

\[
\hat{H}_0 = e^{-i \varphi} H_0 e^{i \varphi} + \partial_t \varphi,
\]

\[
\varphi = \sum_\beta e_\beta \int_0^1 du \vec{x}_\beta \cdot \vec{A}(\vec{R}_G + u \vec{x}_\beta)
\]

\[
= \sum_\beta e_\beta [x^i_\beta A^i + x^j_\beta x^j_\beta A^i_/2],
\]

(88)

\[
\hat{\pi}_\beta^i = p_\beta^i - e_\beta A^i(\vec{r}_\beta)
\]

\[
= p_\beta^i - e_\beta [A^i + x^j_\beta A^j],
\]

(89)

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

\[
e^{-i \varphi} \pi^i_a e^{i \varphi} = p^i_a + \frac{\epsilon_a}{2} (\vec{x}_a \times \vec{B})^j,
\]

(90)

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

(91)

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

(92)
where $\vec{D}$ is the total electric dipole moment $\vec{D} = \sum_\beta e_\beta \vec{x}_\beta$ and we assumed that $\sum_\beta e_\beta = 0$, so the molecule is neutral. In consequence, the transformed Hamiltonian does not depend on $\vec{R}_G$, thus we are allowed to set $\vec{P}_G = 0$. In order to further simplify, we perform the next transformation as defined in Eq. (10), neglect $O(m/M)^2$ terms, and the transformed Hamiltonian takes the form

$$H_0 = H_{el} + H_n + H_\mu + H_\chi,$$

$$H_\mu = -\sum_a \frac{e}{2m} \vec{x}_a \times \vec{q}_a \cdot \vec{B} + \delta H_\mu,$$

$$\delta H_\mu = -\left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) \vec{D} \times \vec{P} \cdot \vec{B} - \frac{1}{2} \left(\frac{1}{m_A} + \frac{1}{m_B}\right) (e_A \epsilon_B^2 + e_B \epsilon_A^2) \vec{R} \times \vec{P} \cdot \vec{B} + \frac{1}{2} \left(\frac{\epsilon_A^2}{m_A} + \frac{\epsilon_B^2}{m_B}\right) \vec{D} \times \sum_a \vec{q}_a \cdot \vec{B} + \frac{\epsilon_A \epsilon_B}{2} \left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) \vec{R} \times \sum_a \vec{q}_a \cdot \vec{B},$$

$$H_\chi = \sum_a \frac{\epsilon_A^2}{8m} (\vec{x}_a \times \vec{B})^2 + \delta H_\chi,$$

$$\delta H_\chi = \frac{1}{8m_A} (e_A \vec{x}_A \times \vec{B} + e_A \vec{D} \times \vec{B})^2 + \frac{1}{8m_B} (e_B \vec{x}_B \times \vec{B} + e_B \vec{D} \times \vec{B})^2.$$

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 has been first investigated by Wick in [20] for H$_2$, later by Ramsey in who extended Wick’s result to arbitrary masses of nuclei and performed first measurements in Ref. [21] and improved measurements with Harrick in Ref. [22]. The rotational magnetic moments result from coupling of the molecular rotation to the magnetic field. The expectation value on the $\Sigma$ state of the first term in Eq. (94) $e/(2m) \vec{J}_{el}$, $\vec{B}$ vanishes, thus the leading coupling comes from nonadiabatic corrections to the matrix element as given by Eq. (13) and from $\delta H_\mu$, namely

$$\gamma_I = \left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) \frac{\vec{D}_{el} \cdot \vec{R}}{R^2} + \frac{e}{2m} \frac{1}{m_a} \frac{1}{m_b} \left\langle \phi_{el} | \vec{J}_{el} \left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) \vec{J}_{el} | \phi_{el} \right\rangle.$$

(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 $\mu_I$ becomes

$$\gamma_I \mu_I \mu = \frac{\mu_I}{J_{\mu I}} = m_n m_p \left(\frac{Z_A}{m_A^2} + \frac{Z_B}{m_B^2}\right) + \frac{m_p}{m_n} \frac{m_r}{m_b} \left\langle \phi_{el} | \vec{J}_{el} \left(\frac{\epsilon_A}{m_A} - \frac{\epsilon_B}{m_B}\right) \vec{J}_{el} | \phi_{el} \right\rangle,$$

(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 depends on the distance $R$ between nuclei. For large $R$ it vanishes at least with $R^{-6}$. The dependence of $\gamma J$ 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, up to our knowledge, have not yet been investigated in the literature and may play a role in the astrophysical environment, however 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 $\chi$. In the BO approximation $\chi_{\text{el}}$ is given by

$$\chi_{\text{el}}^{ij} = -\frac{e^2}{4m} \sum_a \langle \phi_{\text{el}} | x_a^2 J_a^{ij} - x_a^i x_a^j | \phi_{\text{el}} \rangle - \frac{e^2}{2m^2} \langle \phi_{\text{el}} | J_{\text{el}}^i \frac{1}{(E_{\text{el}} - H_{\text{el}})^{1/2}} J_{\text{el}}^j | \phi_{\text{el}} \rangle. \quad (100)$$

For $\Sigma$ states it can be simplified to the form

$$\chi_{\text{el}}^{ij} = -\frac{e^2}{8m} \sum_a \left[ 2 \langle \phi_{\text{el}} | x_a^2 (\vec{n} \cdot \vec{x}_a)^2 | \phi_{\text{el}} \rangle n^i n^j + \langle \phi_{\text{el}} | x_a^2 (\vec{n} \cdot \vec{x}_a)^2 | \phi_{\text{el}} \rangle (\delta^{ij} - n^i n^j) 
- \frac{e^2}{4m^2} \langle \phi_{\text{el}} | J_{\text{el}} \frac{1}{(E_{\text{el}} - H_{\text{el}})^{1/2}} J_{\text{el}} | \phi_{\text{el}} \rangle (\delta^{ij} - n^i n^j) \right]. \quad (101)$$

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 Authors of [23], this second order matrix element with $J_{\text{el}}$ operator, is present also in the nonadiabatic equation for the nuclear function $\chi$ 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]

$$\delta H = \sum_{\alpha, \beta} \frac{e_\alpha e_\beta}{4\pi} \frac{1}{2 r_{\alpha\beta}^3} \left[ g_\alpha \frac{m_\alpha m_\beta}{m_\alpha} \vec{s}_\alpha \cdot \vec{r}_{\alpha\beta} \times \vec{\pi}_\beta - \frac{(g_\alpha - 1)}{m_\alpha^2} \vec{s}_\alpha \cdot \vec{r}_{\alpha\beta} \times \vec{\pi}_\alpha \right]. \quad (102)$$
where summation over $\alpha, \beta$ 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

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

(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. (88,10), and ob tain

$$
\delta H = - \sum_b \frac{e_A e}{4 \pi} \frac{\vec{I}}{2 m_A x_b^2} \cdot \left[ \frac{g_A}{m} \left( \vec{q}_b + \frac{m}{m_A} \vec{P} + \frac{e}{2} \vec{x}_b \times \vec{B} \right) - \frac{(g_A - 1)}{m_A} \left( \vec{P} - \vec{q}_{\text{el}} + \frac{\vec{D}}{2} \times \vec{B} \right) \right]
$$

$$
- \frac{e_A e_B}{4 \pi} \frac{\vec{I}}{2 m_A} \times \frac{\vec{R}}{R^3} \cdot \left[ \frac{g_A}{m_B} \left( \vec{P} + \frac{e_B}{2} \vec{R} \times \vec{B} \right) + \frac{(g_A - 1)}{m_A} \left( \vec{P} - \vec{q}_{\text{el}} + \frac{\vec{D}}{2} \times \vec{B} \right) \right],
$$

(104)

where $\vec{q}_{\text{el}} = \sum_a \vec{q}_a$, $\vec{x}_{\text{el}} = \sum_a \vec{x}_a$, and the electric dipole operator is $\vec{D} = e \vec{x}_{\text{el}} - e_B \vec{R}$. This Hamiltonian will be used in next sections to rederive the known formulæ 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 $m_e/m_n$ what 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 Froesch 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 $\delta H$ above with $\vec{B} = 0$. For considered $\Sigma$ states terms with $\vec{q}_{\text{el}}$ vanish and $\delta H$ takes the form

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

(105)

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

(106)

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

(107)
The expectation value of \( \langle \phi_{el} | \vec{Q}_1 | \phi_{el} \rangle \) vanishes, and \( \vec{Q}_1 \) operator contributes only through nonadiabatic matrix elements Eq. (43), so the total spin-rotation constant is given by

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

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

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

and thus \( \eta \) in atomic units becomes

\[
\eta = \alpha^2 \left[ \frac{1}{R^2} \frac{Z_A g_A}{2 m_n m_A} \sum_a \vec{x}_a \times \vec{q}_a \sum_b \frac{1}{(\mathcal{E}_{el} - H_{el})'} \frac{\vec{x}_b \times \vec{q}_b}{x_b^3} | \phi_{el} \rangle \right.
\]

\[
+ \left. \frac{1}{R} \frac{1}{2 m_A^2} \frac{\partial \mathcal{E}_{el}}{\partial R} + \frac{1}{R^3} \frac{Z_A Z_B g_A}{2 m_A m_n} \right], \tag{110}
\]

in agreement with Ref. [30], their \( C \) is related to our \( \eta \) by \( C = 2\pi \eta \). Since, there is cancellation between the first and the third term, \( \eta \) vanishes at least 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 with the external magnetic field. Here we rederive his result and in addition to it, obtain nonadiabatic corrections. A similar calculations for atoms have 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 \( \delta H \) in Eq. (103). In the BO approximation \( \hat{\sigma}_{el}^{(0)} \) is a sum of diamagnetic and paramagnetic parts. In atomic units, they are correspondingly

\[
\vec{I} \hat{\sigma}_{el}^{(0)} \vec{B} = \alpha^2 \left[ - \frac{1}{2} \langle \phi_{el} | \sum_b \left( \vec{I} \times \frac{\vec{x}_b}{x_b^3} \right) \cdot (\vec{x}_b \times \vec{B}) | \phi_{el} \rangle \right.
\]

\[
+ \langle \phi_{el} | \sum_a \vec{x}_a \times \vec{q}_a \cdot \vec{B} \frac{1}{(\mathcal{E} - H_{el})'} \sum_b \frac{\vec{x}_b \times \vec{q}_b}{x_b^3} \cdot \vec{I} | \phi_{el} \rangle \right]. \tag{111}
\]

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

\[
\hat{\sigma}_{el}^{(1)} = \hat{\sigma}_{n}^{(1)} + \hat{\sigma}_{d}^{(1)} + \hat{\sigma}_{s}^{(1)} + \hat{\sigma}_{l}^{(1)}. \tag{112}
\]
\( \hat{\sigma}^{(1)}_a \) is the correction due to \( H_n \) to the matrix elements in Eq. (111), namely using Eq. (39) one obtains

\[
\begin{align*}
\tilde{I} \hat{\sigma}^{(1)}_a \tilde{B} &= \alpha^2 \left[ -\langle \phi_{el} | \sum_b \left( \tilde{I} \times \frac{\tilde{x}_b}{x_b^3} \right) \cdot (\tilde{x}_b \times \tilde{B}) \frac{1}{(E - H_{el})'} H_n | \phi_{el} \rangle \\
+ \langle \phi_{el} | \sum_b \tilde{x}_a \times \tilde{q}_a \cdot \tilde{B} \frac{1}{(E - H_{el})'} (H_n - E_{a}) \left( \frac{1}{(E - H_{el})'} \sum_b \tilde{x}_b \times \tilde{q}_b \cdot \tilde{I} \right) | \phi_{el} \rangle \\
+ \langle \phi_{el} | \tilde{H}_n \left( \frac{1}{(E - H_{el})'} \sum_b \tilde{x}_a \times \tilde{q}_a \cdot \tilde{B} \right) \frac{1}{(E - H_{el})'} \sum_b \tilde{x}_b \times \tilde{q}_b \cdot \tilde{I} \left( \frac{1}{(E - H_{el})'} \tilde{H}_n \right) | \phi_{el} \rangle \right].
\end{align*}
\]

(113)

\( \hat{\sigma}^{(1)}_d \) is a correction to the diamagnetic part due to the direct coupling of the nuclear spin to the magnetic field in \( \delta H \), Eq. (104)

\[
\begin{align*}
\tilde{I} \hat{\sigma}^{(1)}_d \tilde{B} &= \frac{\alpha^2}{2g_A} \langle \phi_{el} | \frac{(g_A - 1)}{m_A} \sum_b \left( \tilde{I} \times \frac{\tilde{x}_b}{x_b^3} \right) \cdot (\tilde{x}_b + Z_B \tilde{R}) \times \tilde{B} \\
- \left( \tilde{I} \times \frac{\tilde{R}}{R^3} \right) \cdot \left[ \frac{Z_B}{m_B} \tilde{R} - \frac{Z_B (g_A - 1)}{m_A} (\tilde{x}_b + Z_B \tilde{R}) \right] \times \tilde{B} \langle \phi_{el} \rangle.
\end{align*}
\]

(114)

\( \hat{\sigma}^{(1)}_s \) is a correction to paramagnetic part due to spin-rotation interaction in \( \delta H \) Eq. (104)

\[
\begin{align*}
\tilde{I} \hat{\sigma}^{(1)}_s \tilde{B} &= \frac{\alpha^2}{g_A} \langle \phi_{el} | \sum_a \tilde{x}_a \times \tilde{q}_a \cdot \tilde{B} \frac{1}{(E - H_{el})'} \left( \frac{1}{m_A} \sum_b \tilde{x}_b \times \frac{1}{x_b^3} \times \left[ \tilde{P} + (g_A - 1) \tilde{q}_a \right] \\
- Z_B \tilde{R} \times \left[ \frac{g_A}{m_B} \tilde{P} + \left( \frac{g_A - 1}{m_A} \right) (\tilde{P} - \tilde{q}_a) \right] \right) | \phi_{el} \rangle.
\end{align*}
\]

(115)

The derivative over nuclear coordinates \( \tilde{P} \) in the above and below, can act on the right or on the left, since these matrix elements does not depend on this. Finally, \( \hat{\sigma}^{(1)}_1 \) is a correction to the paramagnetic part due to \( \delta H_\mu \) in Eq. (93),

\[
\begin{align*}
\tilde{I} \hat{\sigma}^{(1)}_1 \tilde{B} &= \alpha^2 \langle \phi_{el} | \left\{ \frac{1}{m_A} (\tilde{x}_e + Z_B \tilde{R}) \times (2 \tilde{P} - \tilde{q}_a) - \frac{Z_B}{m_n} \tilde{R} \times \tilde{P} \right\} \cdot \tilde{B} \\
&\frac{1}{(E - H_{el})'} \sum_b \tilde{x}_b \times \tilde{q}_b \cdot \tilde{I} | \phi_{el} \rangle.
\end{align*}
\]

(116)

The total magnetic shielding \( \hat{\sigma} \) is obtained by averaging with the nuclear wave function

\[
\sigma^{ij} = \langle \chi | \sigma_{el}^{(0)ij} + \sigma_{el}^{(1)ij} | \chi \rangle,
\]

(117)

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

\[
\delta \sigma^{ij} = \frac{2}{\gamma_I} \langle \chi | \eta J^i \frac{1}{E_a - H_n - E_{a} - E_{el}} \gamma_L J^j | \chi \rangle,
\]

(118)
which however is negligible.

Let us present in more details the averaged shielding \( \sigma = \sigma^{ii}/3 \) in the case of \( \text{H}_2 \) and isotopomers \( Z_A = Z_B = 1 \),

\[
\sigma = \langle \chi | \sigma_{el}^{(0)} + \sigma_{el}^{(1)} | \chi \rangle, 
\]

and

\[
\sigma_{el}^{(0)} = \frac{\alpha^2}{3} \left[ \langle \phi_{el} | \sum_b \frac{1}{x_b} | \phi_{el} \rangle + \langle \phi_{el} | \sum_a \bar{x}_a \times \bar{q}_a \frac{1}{(E - H_{el})'} \sum_b \bar{x}_b \times \bar{q}_b \frac{1}{x_b^3} | \phi_{el} \rangle \right] ,
\]

\[
\sigma_{el}^{(1)} = \frac{\alpha^2}{3} \left[ 2 \langle \phi_{el} | \sum_b \frac{1}{x_b} \frac{1}{(E - H_{el})'} \bar{H}_n \ | \phi_{el} \rangle + \langle \phi_{el} | \sum_a \bar{x}_a \times \bar{q}_a \frac{1}{(E - H_{el})'} \sum_b \bar{x}_b \times \bar{q}_b \frac{1}{x_b^3} | \phi_{el} \rangle \right] ,
\]

\[
\sigma_{d}^{(1)} = -\frac{\alpha^2}{3 g_A} \langle \phi_{el} | \frac{(g_A - 1)}{m_A} \sum_b \frac{\bar{x}_b}{x_b^3} \cdot (\bar{x}_el + \bar{R}) \right] - \frac{1}{m_B R} | \phi_{el} \rangle ,
\]

\[
\sigma_{s}^{(1)} = \frac{\alpha^2}{3 g_A} \langle \phi_{el} | \sum_a \bar{x}_a \times \bar{q}_a \frac{1}{(E - H_{el})'} \left\{ \frac{1}{m_A} \sum_b \frac{\bar{x}_b}{x_b^3} \times \frac{1}{m_B R} \right\} | \phi_{el} \rangle ,
\]

\[
\sigma_{1}^{(1)} = \frac{\alpha^2}{3} \langle \phi_{el} \left[ \frac{1}{m_A} (\bar{x}_el + \bar{R}) \times (2 \bar{P} - \bar{q}_{el}) \right] - \frac{1}{m_n} \bar{R} \times \bar{P} \right] \frac{1}{(E - H_{el})'} \sum_b \frac{\bar{x}_b \times \bar{q}_b}{x_b^3} | \phi_{el} \rangle .
\]

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 \( \text{H}_2 \) and isotopomers.

VII. SUMMARY

We have presented a general approach to finite nuclear mass corrections in molecular properties which is based on the nonadiabatic perturbation theory [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$_2$ 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. Finally, we presented nonadiabatic corrections to the magnetic shielding, which are important for molecules involving hydrogen or deuterium, where the finite nuclear mass significantly affects the magnetic shielding.

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We are aware of the unpublished PhD work of Charles Harisson Hunt, under supervision of R.V. Reid, University of California (1980). In this work some of nonadiabatic corrections are derived but the result is far from being complete.

The definition of the g-factor assumed here is different from the standard one by the use of the actual charge $e$ and the mass $m$ of the corresponding particle, namely the coupling of the spin to the magnetic field is $-e g/(2m) \vec{s} \cdot \vec{B}$.