Rovibrational levels of HD†

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The dissociation energies of all rotation–vibrational states of the molecular HD in the ground electronic state are calculated to a high accuracy by including nonadiabatic, relativistic $x^2$, and quantum electrodynamic $x^3$ effects, with approximate treatment of small higher order $x^4$, and finite nuclear size corrections. The obtained result for the ground molecular state of $36\ 405.7828(10)$ cm$^{-1}$ is in a small disagreement with the latest most precise experimental value.

I. Introduction

Since the beginning of quantum mechanics molecular hydrogen and its isotopomers have been a ground for testing and developing experimental techniques and theoretical models. In determination of the dissociation energy ($D_0$), experimental and theoretical measurements have diminished their individual uncertainties to below $10^{-3}$ cm$^{-1}$ and are in good agreement. In particular, the latest theoretical $D_0 = 36\ 118.0696(7)$ cm$^{-1}$ of H$_2$, obtained by Piszczatowski et al., agrees very well with $36\ 118.0696(7)$ cm$^{-1}$ derived experimentally by Liu et al.$^2$ Analogous results obtained last year for D$_2$ are $36\ 748.3633(9)$ cm$^{-1}$ from theory$^1$ and $36\ 748.3628(60)$ cm$^{-1}$ from experiment.$^3$ The tiny difference of $0.0004$ cm$^{-1}$ fits well within both error estimates. To achieve this $10^{-3}$ cm$^{-1}$ level of accuracy, the theory must have taken into account, with sufficient precision, not only the electron correlation but also the finite nuclear mass, relativistic, and quantum electrodynamics (QED) effects.

Particularly challenging is the accurate inclusion of nonadiabatic effects. One possible approach is to obtain a nonadiabatic wave function (depending explicitly on nuclear coordinates) by minimizing the nonrelativistic energy. For H$_2$ such calculations, using explicitly correlated James–Coolidge functions, were attempted by Kolos and Wolniewicz in 1963$^4,5$ and 15 years later by Bishop and Cheung.$^6$ The same authors performed purely nonadiabatic calculations for HD. Kolos and Wolniewicz obtained $D_0 = 36\ 402.4$ cm$^{-1}$ whereas Bishop and Cheung reported $D_0 = 36\ 405.97$ cm$^{-1}$.$^7$ Calculations in a similar spirit, but using extensively optimized explicitly correlated Gaussian functions, were performed by Stanke et al.$^8$ Their nonadiabatic wave function was further employed to compute perturbatively the relativistic correction to the nonadiabatic energy. An apparent drawback of these methods is their decreasing accuracy observed for the higher excited states, particularly those lying close to dissociation threshold. For such states the perturbative treatment of relativistic effects may be inadequate. As an example, the $v = 14, J = 4$ state of H$_2$ becomes a resonance after the inclusion of relativistic effects on the level of the potential energy curve (PEC). Moreover, certain properties like the ortho–para mixing or the scattering length, are inaccessible within the direct nonadiabatic approach.

In contrast, the nonadiabatic perturbation theory (NAPT) approach employed here, relies on solving the radial, variable-mass Schrödinger equation with the PEC for the nuclei constructed from the adiabatic potential augmented by $R$-dependent nonadiabatic, relativistic and QED corrections. The theory of the nonadiabatic potentials has been developed in ref. 10 and 11, whereas the relativistic and QED corrections to the PEC are evaluated on the basis of the nonrelativistic quantum electrodynamics (NRQED).$^{12–14}$ These corrections are unambiguously identified by an expansion of a bound atomic or molecular state energy in powers of the fine structure constant $\alpha$:

$$E = E^{(0)} + x^2 E^{(2)} + x^3 E^{(3)} + x^4 E^{(4)} + \cdots,$$

(1)

where $E^{(3)}$ and higher order terms may additionally depend on $\ln x$. The first term of the expansion represents the nonrelativistic energy, $x^2 E^{(2)}$ is the leading relativistic contribution, terms proportional to $x^3$ and $x^4$ describe the QED effects of the leading and higher order, respectively. In this paper we report on application of this approach to all rovibrational levels of the ground electronic state of HD molecule. Uncertainty of our results comes mainly from the neglect of the finite nuclear mass corrections of the order $x^2 m/M$ to the relativistic contribution to the PEC, and from the approximate treatment of the $x^3$ correction. The neglect of higher order nonadiabatic terms proportional to $(m/M)^3$ also increases the overall uncertainty.

II. Nonrelativistic Hamiltonian

We consider a two-electron diatomic molecule in the reference frame attached to the geometrical center of the two nuclei. The total wave function $\phi$ is a solution of the stationary Schrödinger equation

$$H \phi = E \phi,$$

(2)

with the Hamiltonian

$$H = H_{el} + H_{in},$$

(3)

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split into the electronic and nuclear parts. In the electronic Hamiltonian

\[ H_{el} = -\sum_a \frac{\nabla_a^2}{2m_e} + V, \]  

(4)

where \( V \) is the Coulomb interaction

\[ V = -\frac{1}{r_{1a}} - \frac{1}{r_{1b}} - \frac{1}{r_{2a}} - \frac{1}{r_{2b}} + \frac{1}{r_{12}} + \frac{1}{R}, \]  

(5)

the nuclei have fixed positions \( \vec{R}_A \) (proton) and \( \vec{R}_B \) (deuteron), and \( R = \vec{R}_A - \vec{R}_B \). The nuclear Hamiltonian is

\[ H_n = -\frac{\nabla_R^2}{2\mu_n} - \frac{\nabla_{el}^2}{2\mu_n} - \left( \frac{1}{M_A} - \frac{1}{M_B} \right) \nabla_R \cdot \nabla_{el} \]
\[ = H_n' + H_n'', \]  

(6)

where \( \nabla_{el} = \frac{1}{2} \sum_a \nabla_a \), \( \mu_n = (1/M_A + 1/M_B)^{-1} \) is the nuclear reduced mass, and \( H_n', H_n'' \) are even and odd parts with respect to the inversion.

In order to simplify the calculation of nonadiabatic corrections we introduce a unitary transformation

\[ \hat{H} = U^+ H U \]  

(7)

of the form

\[ U = e^{i\vec{r} \cdot \nabla_R} \]  

(8)

with \( \vec{r} = \sum_a \vec{r}_a \) and the nuclear mass asymmetry parameter

\[ \lambda = -\frac{m_e}{2} \left( \frac{1}{M_B} - \frac{1}{M_A} \right). \]  

(9)

The transformed Hamiltonian is

\[ \hat{H} = H + \lambda [H, \vec{r} \cdot \nabla_R] + \frac{j^2}{2} \left[ [H, \vec{r} \cdot \nabla_R], \vec{r} \cdot \nabla_R \right] + \mathcal{O}(\lambda^3), \]  

(10)

where the higher order terms in the electron–nuclear mass ratio \( \mathcal{O}(m_e/M_{A,B})^3 \) are neglected, so that

\[ \hat{H} = H_{el} + H_n' + \lambda [V, \vec{r} \cdot \nabla_R] \]
\[ + \frac{j^2}{2 m_e} [\nabla_{el} \cdot \vec{r} \cdot \nabla_R, \vec{r} \cdot \nabla_R] + \frac{j^2}{2} [H_{el}, \vec{r} \cdot \nabla_R], \vec{r} \cdot \nabla_R], \]  

(11)

and the \( \mathcal{O}(m_e/M_{A,B})^3 \) terms are neglected as well. The internal commutator in the last term of eqn (11) is

\[ [H_{el}, \vec{r} \cdot \nabla_R] = -\vec{r} \cdot \nabla_R(V) - \frac{2}{m_e} \nabla_{el} \cdot \vec{r} \cdot \nabla_R, \]  

(12)

so that the transformed Hamiltonian can be decomposed as

\[ \hat{H} = H_{el} + H_n' + \hat{H}_n'', \]  

(13)

where

\[ \hat{H}_n' = H_n' + \lambda^2 \left[ \frac{1}{m_e} \nabla_{el} \cdot \nabla_R - \frac{1}{2} \vec{r} \cdot \nabla_R(V), \vec{r} \cdot \nabla_R \right] \]
\[ = H_n' + \lambda^2 \nabla_R^2 + \frac{j^2}{2} \nabla_{el} \nabla_R(V) \]
\[ \hat{H}_n'' = -\lambda \vec{r} \cdot \nabla_R(V). \]  

(14)

Both the nuclear Hamiltonians involve the derivative of the Coulomb operator \( V \), which is

\[ \nabla_R(V) = \frac{1}{2} \left( \frac{\vec{r}_{1A}}{r_{1A}^3} + \frac{\vec{r}_{1B}}{r_{1B}^3} - \frac{\vec{r}_{2A}}{r_{2A}^3} - \frac{\vec{r}_{2B}}{r_{2B}^3} \right) - \frac{n}{R^2} \]  

(16)

with \( n = \vec{R}/R \), while the second derivative of \( V \) is further transformed in eqn (47)–(49).

III. Adiabatic approximation

In the adiabatic approximation the total wave function of the molecule

\[ \phi_a(\vec{r}, \vec{R}) = \phi_{el}(\vec{r})\chi(\vec{R}) \]  

(17)

is represented as a product of the electronic wave function \( \phi_{el} \) and the nuclear wave function \( \chi \). The electronic wave function obeys the clamped nuclei electronic Schrödinger equation

\[ [H_{el} - \varepsilon_{el}(R)]\phi_{el} = 0, \]  

(18)

while the wave function \( \chi \) is a solution to the nuclear Schrödinger equation with the effective potential generated by electrons

\[ \left[ -\nabla_R^2 + \varepsilon_a(R) + \varepsilon_{el}(R) - E_a \right] \chi = 0, \]  

(19)

where \( \varepsilon_a(R) \) is the so-called adiabatic (or diagonal) correction defined as

\[ \varepsilon_a(R) = \langle \phi_{el} | H_n'| \phi_{el} \rangle \]  

\[ = \frac{1}{2\mu_n} \langle \nabla_R \phi_{el} | \nabla_R \phi_{el} \rangle - \langle \phi_{el} | \nabla_{el}^2 \phi_{el} \rangle. \]  

(20)

Separation of the angular variables in eqn (19) leads to the well-known radial nuclear equation

\[ \left[ -\frac{1}{R^2} \frac{\partial}{\partial R} R^2 \frac{\partial}{\partial R} + \frac{J(J+1)}{2R^2} + \varepsilon_{el}(R) + \varepsilon_a(R) \right] \chi_J(R) \]
\[ = E_a \chi_J(R). \]  

(21)

Solving this equation gives an adiabatic energy level \( E_a \) and an adiabatic radial nuclear wave function \( \chi_J \).
IV. Nonadiabatic nuclear Schrödinger equation

Following the NAPT formalism introduced recently,\textsuperscript{10,11} we can obtain energy levels $E$ including leading nonadiabatic corrections by solving the following nonadiabatic version of the radial Schrödinger equation

$$\left[ \frac{1}{R^2} \frac{\partial}{\partial R} \left( \frac{R^2}{2\mu} \frac{\partial}{\partial R} \right) + \frac{J(J+1)}{2\mu} + \mathcal{V}(R) \right] \psi_J(R) = E \psi_J(R),$$

(22)

where $\mathcal{V}(R)$ is a nonadiabatic potential energy function. In the nonrelativistic limit

$$\mathcal{V}(R) = \mathcal{V}_{\text{el}}(R) + \mathcal{V}_{\text{na}}(R) + \mathcal{V}_{\text{el}}(R) + \mathcal{V}_{\text{na}}(R),$$

(23)

with the nonadiabatic correction constructed from the homonuclear part $\delta\mathcal{V}_{\text{na}}(R)$, defined in our previous work on H\textsubscript{2},\textsuperscript{10,11} and the heteronuclear part proportional to $\lambda^2$

$$\delta\mathcal{V}_{\text{na}} = \lambda^2 \left[ \left\langle \phi_{\text{el}} \left| \frac{1}{2m_e} \mathcal{V}_{\text{R}}^2 + \frac{1}{4m_e} \frac{\partial^2}{\partial R^2} \mathcal{V}_{\text{R}}^2 \right| \phi_{\text{el}} \right\rangle_{\text{el}} + \left\langle \phi_{\text{el}} \left| \frac{1}{\mathcal{V}_{\text{el}} - \mathcal{V}_{\text{el}}} \mathcal{V}_{\text{R}} \right| \phi_{\text{el}} \right\rangle_{\text{el}} \right],$$

(24)

which is obtained from eqn (14) and (15). Apart from the nonadiabatic potential $\mathcal{V}(R)$, the difference between eqn (22) and (21) lies in the effective masses used. In the adiabatic eqn (21) the reduced nuclear mass $\mu$, appearing in both translational and rotational kinetic terms is a constant, while in the nonadiabatic eqn (22) it is given by two different functions of the internuclear distance. These two effective reduced mass functions

$$\frac{1}{2\mu} = \frac{1}{2\mu} + \mathcal{V}_{\parallel}(R) - \frac{\lambda^2}{m_e}$$

(25)

$$\frac{1}{2\mu} = \frac{1}{2\mu} + \mathcal{V}_{\perp}(R) - \frac{\lambda^2}{m_e}$$

(26)

are defined with the help of additional radial functions

$$\mathcal{V}_{\parallel}(R) = \frac{1}{\mu} \left\langle n \cdot \mathcal{V}_{\text{R}} \phi_{\text{el}} \left| \frac{1}{\mathcal{V}_{\text{el}} - \mathcal{V}_{\text{el}}} \mathcal{V}_{\text{R}} \phi_{\text{el}} \right\rangle_{\text{el}} \right.$$ (27)

and

$$\mathcal{V}_{\perp}(R) = \frac{1}{2\mu} \left( \delta_{\parallel}^2 - \delta_{\parallel}^2 \right) \left\langle \mathcal{V}_{\text{R}} \phi_{\text{el}} \left| \frac{1}{\mathcal{V}_{\text{el}} - \mathcal{V}_{\text{el}}} \mathcal{V}_{\text{R}} \phi_{\text{el}} \right\rangle_{\text{el}} \right.$$ (28)

In total, three radial functions are needed to construct the nonadiabatic radial Schrödinger eqn (22) for diatomic molecules: two functions, defined by eqn (27) and (28), to describe the variable effective reduced masses of eqn (25) and (26), and the nonadiabatic potential $\mathcal{V}$. This potential, in turn, is expressed by another four functions: BO energy $\mathcal{V}_{\text{el}}$, adiabatic $\mathcal{V}_{\text{el}}$, nonadiabatic homonuclear $\delta\mathcal{V}_{\text{na}}$ and heteronuclear $\delta\mathcal{V}_{\text{na}}$ corrections (see eqn (23)).

V. Separated atoms limit

At large internuclear distances the effective reduced mass functions (25) and (26) are expected to approach a value corresponding to the reduced mass of separate H and D atoms

$$\frac{1}{\mu} = \frac{1}{m_p + m_e} + \frac{1}{m_d + m_e},$$

(29)

Because $\mathcal{V}_{\parallel}(R)$ and $\mathcal{V}_{\perp}(R)$ tend to $-\frac{m_e(4\mu)^2}{m_e}$, when $R \to \infty$, we have

$$\frac{1}{2\mu} = \frac{1}{2m_p} = \frac{1}{2\mu_p} - \frac{\lambda^2}{m_e}$$

(30)

$$\frac{1}{2\mu} = \frac{1}{2} \left[ \frac{1}{m_p} \left( 1 - \frac{m_e}{m_p} \right) + \frac{1}{m_d} \left( 1 - \frac{m_e}{m_d} \right) - \ldots \right]$$

(31)

which are exactly the leading terms of the expansion of the atomic reduced mass (29) in the electron–nucleus mass ratio

$$\frac{1}{2\mu} = \frac{1}{2} \left[ \frac{1}{m_p} \left( 1 - \frac{m_e}{m_p} \right) + \frac{1}{m_d} \left( 1 - \frac{m_e}{m_d} \right) - \ldots \right],$$

(32)

In the separated atoms limit, the nonrelativistic energy of the system (the dissociation threshold) $\mathcal{E}(\infty)$ is simply a sum of the energies of hydrogen and deuterium atoms expressed by their reduced masses

$$\mathcal{E}(\infty) = -\frac{\mu_1}{2} - \frac{\mu_2}{2}.$$

(34)

The expansion of $\mathcal{E}(\infty)$ in the electron to nucleus mass ratio is of the form

$$\mathcal{E}(\infty) = -1 + \frac{1}{2} \left( \frac{m_e}{m_p} + \frac{m_e}{m_d} \right) - \frac{1}{2} \left( \frac{m_e^2}{m_p^2} + \frac{m_e^2}{m_d^2} \right) + \ldots.$$ (35)

Subsequent terms of this expansion coincide with the $R \to \infty$ limits of corresponding components of the nonadiabatic potential $\mathcal{V}(R)$ of eqn (23),

$$\mathcal{V}_{\text{el}}(\infty) = -1,$$ (36)

$$\mathcal{V}_{\text{el}}(\infty) = \frac{m_e}{2\mu_n},$$ (37)

$$\mathcal{V}_{\text{el}}(\infty) = \frac{m_e}{2\mu_p},$$ (38)

$$\mathcal{V}_{\text{el}}(\infty) = -\frac{\lambda^2}{m_e}.$$ (39)

In particular, the sum of eqn (38) and (39) is equal to the third term in the expansion (35).

VI. Relativistic and radiative corrections

The relativistic correction to the adiabatic potential for a singlet state is given by the expectation value with the
The relativistic and QED corrections can be computed directly, as expectation values with the adiabatic wave function. It is more convenient and more accurate, however, to include them into the nonadiabatic Schrödinger eqn (22) by adding pertinent radial functions into the $\Psi(R)$ potential (23). In such an approach, the eigenvalue of the Schrödinger equation represents a total energy including all the mentioned finite nuclear mass, relativistic and QED effects.

VII. Computational details

The radial nonadiabatic eqn (22), apart from the clamped nuclei energy $\delta E_{cl}$ and the adiabatic correction $\delta E_{ad}$, involves $\Psi^<, \Psi^>$, and the potentials $\delta E_{na}$ and $\delta E_{na}$ in eqn (24). The numerical values for all but the last radial functions were obtained for H2 and a simple rescaling by the first or second power of the reduced mass ratio converts them to the pertinent HD functions. For this reason, we shall omit a detailed description of how these functions were obtained, referring the reader to our previous work on H2.10,11 Below we give only basic information on these functions and then concentrate on the new terms which result from the nuclear mass asymmetry in HD.

The electronic energy, $\delta E_{el}$, used in this work is exactly the same as the one reported in ref. 1. Its analytic form is based on the energy points calculated by Sims and Hagstrom22 using Hylleraas wave function and by Cencek23 using an explicitly correlated Gaussian (ECG) wave function. The relative accuracy of these calculations is of the order of 10~12, which corresponds to about 10~10 of the relative accuracy of the Born–Oppenheimer potential. The ground state dissociation energy obtained by numerically solving the adiabatic Schrödinger eqn (21) in the Born–Oppenheimer approximation with this analytic potential is 36401.93319 cm~1 (see also Table 1). Also the relativistic and QED corrections to the potential obtained for H2 in ref. 1 apply directly to HD because they do not depend on the nuclear mass.

The adiabatic correction $\delta E_{ad}$ has been evaluated analytically by means of a new method described in ref. 10 and 11. The radial function $\delta E_{ad}$ previously obtained for H2 has been rescaled to HD by the ratio of the reduced masses of nuclei $\mu_{H2}/\mu_{HD}$

$$\delta E_{ad}^{HD} = \frac{\mu_{HD}}{\mu_{H2}} \delta E_{ad}^{H2}$$

and led to the adiabatic dissociation energy of the ground state equal to 36 406.18407 cm~1.

Similarly, the nonadiabatic potentials $\delta E_{na}, \Psi^<$, and $\Psi^>$ were obtained for H2 in ref. 11 and here are rescaled to HD by the square of the reduced mass ratio $(\mu_{H2}/\mu_{HD})^2$. Numerical

Table 1 Components of $D_0$ (in cm~1) for $\nu = 0, J = 0$ state of HD. Uncertainties of $x^2$ and $x^4$ come from the neglect of nuclear recoil corrections and that of $x^6$ from the approximate formula

<table>
<thead>
<tr>
<th>Component</th>
<th>$D_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BO</td>
<td>36 401.9332(1)</td>
</tr>
<tr>
<td>Adiabatic correction</td>
<td>4.2509(1)</td>
</tr>
<tr>
<td>Nonadiabatic correction</td>
<td>0.3267(2)</td>
</tr>
<tr>
<td>$x_0^6$ subtotal</td>
<td>36 406.5108(2)</td>
</tr>
<tr>
<td>$x_0^8$ correction</td>
<td>0.5299(4)</td>
</tr>
<tr>
<td>$x_0^6$ finite nuclear size correction</td>
<td>0.0001(0)</td>
</tr>
<tr>
<td>$x_0^4 + x_0^6$ subtotal</td>
<td>36 405.9809(5)</td>
</tr>
<tr>
<td>$x_0^4$ correction</td>
<td>0.1964(2)</td>
</tr>
<tr>
<td>$x_0^4$ correction</td>
<td>0.0016(8)</td>
</tr>
<tr>
<td>Total</td>
<td>36 405.7828(10)</td>
</tr>
</tbody>
</table>
values of the nuclear masses \(m_p = 1836.152 672 47 m_e\) and \(m_a = 3670.482 965 4 m_e\) used in this study are based on the CODATA 2006 compilation of fundamental physical constants\(^\text{17}\) and were taken from the NIST Web Page\(^\text{18}\). The nuclear reduced mass of HD is \(\mu_n = 1223.899 2280 m_e\) and the nuclear mass asymmetry parameter \(\lambda = 1.360 866 544 2 \times 10^{-4} m_e\).

The only newly evaluated function of \(R\) is the heteronuclear nonadiabatic correction \(\delta \sigma'_{\text{na}}\), eqn (24), resulting from those terms of the Hamiltonian \(\tilde{H}\), which contain \(\lambda\) [see eqn (14) and (15)]. \(\delta \sigma'_{\text{na}}\) comprises three parts. The first part is analogous to the nuclear kinetic energy term in the adiabatic correction (20) and requires evaluation of the derivative of the electronic wave function over the nuclear variable \(\tilde{R}\). This differentiation can be accomplished with the help of the following formula\(^\text{24}\)

\[
\nabla_{\tilde{R}} \phi_{\text{el}} = \frac{1}{\{E_{\text{el}} - H_{\text{el}}\}} \frac{\partial V}{\partial \tilde{R}} \phi_{\text{el}} - i \nabla_{\tilde{R}} \phi_{\text{el}}.
\]

In the above equation, the first term gives the parallel component and requires an additional basis set of \(1^{\Sigma_u^+}\) symmetry to evaluate the reduced resolvent. The perpendicular component is obtained by evaluation of the expectation value of an operator resulting from the last term, which involves the nuclear angular momentum operator \(L_\text{el} = -i \tilde{R} \times \nabla_{\tilde{R}}\). Here we made use of the following identity valid for the \(\Sigma\) states: \(L_\text{el} \phi_{\text{el}} = -L_\text{el} \phi_{\text{el}}\), where \(L_\text{el}\) is the electronic angular momentum operator \(L_\text{el} = -i \sum_a \tilde{r}_a \times \nabla_a\). In this new formulation, it is possible to avoid the involvement of \(\Pi\) symmetry functions—the perpendicular component is obtained directly from the electronic ground state wave function as

\[
-\frac{1}{R} \langle \phi_{\text{el}} | L_\text{el}^2 | \phi_{\text{el}} \rangle_{\text{el}}.
\]

The second part of \(\delta \sigma'_{\text{na}}\) contains operators which are difficult in numerical evaluation, so we transform it to a more convenient form using the following identity

\[
\nabla_{\tilde{R}} \nabla_{\tilde{R}}(V) = (\nabla_{\tilde{R}} \tilde{R} - \nabla_{\tilde{R}}) (\nabla_{\tilde{R}} V) + \nabla_{\tilde{R}} \nabla_{\tilde{R}} V.
\]

The first term on the right hand side of eqn (47) is

\[
(\nabla_{\tilde{R}} \tilde{R} - \nabla_{\tilde{R}}) (\nabla_{\tilde{R}} V) = \frac{3R^2 \tilde{R}^2 - \delta \tilde{R}^2}{R^2} - \frac{4\pi}{3} \delta \tilde{R}^2 (R),
\]

where the \(\delta \tilde{R}^2\) part can be neglected, while the second term is evaluated using integration by parts

\[
\langle \phi_{\text{el}} | r^2 \nabla_{\tilde{R}} \nabla_{\tilde{R}} V | \phi_{\text{el}} \rangle_{\text{el}} = \int d\tilde{r} \nabla_{\tilde{R}} \nabla_{\tilde{R}} \tilde{r}^2 \phi_{\text{el}}^2.
\]

The third part of the heteronuclear nonadiabatic correction \(\delta \sigma'_{\text{na}}\), eqn (24), is again a second order quantity, which requires evaluation of the resolvent in the basis set of \(1^{\Sigma_u^+}\) symmetry.

All these expectation values as well as the second order quantities were evaluated in the basis of exponentially correlated Gaussians (ECG) functions\(^\text{25}\)

\[
\psi_k(\tilde{r}_1, \tilde{r}_2) = (1 + \tilde{P}_{12}) (1 \pm \tilde{\hat{J}}) \Xi \times \exp \left[ -\sum_{j=1}^{2} A_{k,j} (\tilde{r}_j - \tilde{s}_{k,j}) (\tilde{r}_j - \tilde{s}_{k,j}) \right],
\]

where the matrices \(A_{k}\) and vectors \(\tilde{s}_k\) contain nonlinear parameters, 5 per basis function, to be variationally optimized with respect to either the electronic energy or pertinent Hylleraas functional. The antisymmetry projector \((1 + \tilde{P}_{12})\) ensures singlet symmetry, the spatial projector \((1 \pm \tilde{\hat{J}})\) ensures the gerade (+) or ungerade (−) symmetry, and the \(\Xi_k\) prefactor enforces \(\Sigma\) states when equal to 1, or \(\Pi\) states when equal to \(y_j\) (the perpendicular Cartesian component of the electron coordinate). For the second order matrix elements we generated a 600-term ECG basis set of \(1^{\Sigma_u^+}\) or \(1^{\Sigma_u^+}\) symmetries. The nonlinear parameters of this basis were optimized by minimizing the functional corresponding to this matrix element.

Finally, the total potential \(H\) in the Schrödinger eqn (22) reads

\[
H(R) = \sigma_{\text{el}}(R) + \sigma_{\text{a}}(R) + \delta \sigma_{\text{na}}(R) + \delta \sigma'_{\text{na}}(R) + \delta \sigma^{(2)}(R) + \delta \sigma'^{(2)}(R).
\]

All its components were shifted by subtracting corresponding atomic values (see section V and ref. 1) so that they asymptotically tend to zero.

VIII. Results and discussion

Table I shows the dissociation energy of the ground rovibrational level decomposed into all the known significant contributions. Particular corrections have been computed as a difference between the eigenvalues obtained adding successively corresponding contributions to the potential \(H\), eqn (51). For instance, the \(x^2\) relativistic correction has been evaluated from two eigenvalues: one obtained with \(H = \sigma_{\text{el}} + \sigma_{\text{a}} + \delta \sigma_{\text{na}} + \delta \sigma'_{\text{na}} + \delta \sigma^{(2)}\) and the other with \(H = \sigma_{\text{el}} + \sigma_{\text{a}} + \delta \sigma_{\text{na}} + \delta \sigma'_{\text{na}}\). Relativistic and QED corrections can also be obtained without the nonadiabatic potential \(\delta \sigma_{\text{na}} + \delta \sigma'_{\text{na}}\). The difference for the ground state is quite small \(10^{-6}\) cm\(^{-1}\); however for excited states the difference can be larger.

There are several possible sources of the uncertainty in the final dissociation energy. The three dominating are (i) the missing relativistic and QED recoil terms of \(\mathcal{O}(m/c\mu)\), (ii) the neglect of the nonadiabatic terms of \(\mathcal{O}((m/c\mu)^2)\), and (iii) the approximate treatment of the \(x^2\) contribution. Although the formulas for the omitted relativistic recoil terms are explicitly known\(^\text{24}\) no numerical calculations have been performed so far. The error caused by the neglect of this term can be estimated as \(m/c\mu\) times the \(x^2\) correction (see ref. 1) and, analogously, times the \(x^2\) correction to account for the missing QED recoil term. For \(D_0\) of the ground rovibrational level these two contributions are 0.00043 cm\(^{-1}\) and 0.00016 cm\(^{-1}\), respectively. In a similar fashion, the contribution to the error budget from the missing higher order nonadiabatic terms can be approximated as proportional to \(m/c\mu\) times the second order nonadiabatic correction, which amounts to 0.00026 cm\(^{-1}\) at the ground level. The last meaningful part of the uncertainty results from the incomplete treatment of the higher order QED effects. As previously, (ref. 1) we conservatively estimate that the terms omitted in \(\delta \sigma^{(4)}\), eqn (43), contribute ca. 50% of the one-loop term, which yields 0.0008 cm\(^{-1}\) of the uncertainty.

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The quadratic sum of these four error components leads to the overall uncertainty on the ground state \(D_0\) of less then \(0.0010\) cm\(^{-1}\). For the rotationally and vibrationally excited levels, the uncertainty changes in accord with the size of the corrections. Its estimation for individual levels is listed in the ESI.† In total, there are 400 bound levels with the vibrational quantum number \(v\) ranging from 0 to 17. The number of the rotational levels decreases with growing \(v\) from 37 for \(v = 0\) to only 2 in the highest \(v = 17\) state. The full set of the total dissociation energies is presented in Table 5. Moreover, a detailed specification, similar to that in Table 1, has been prepared for each bound rovibrational level and is available in the ESI.‡ For each combination of the vibrational and rotational quantum numbers there are 8 entries corresponding to: six components of the dissociation energy, the total \(D_0\), and the estimated uncertainty of the total \(D_0\). The six components of the total \(D_0\) are, respectively: the Born–Oppenheimer, adiabatic, nonadiabatic, \(x^2\) relativistic (including finite nuclear size), \(x^4\) QED, and \(x^6\) QED.

Table 2 assembles several experimental and theoretical nonadiabatic values of \(D_0\) obtained over the years for the ground rovibrational level. More details on the progress in determining the dissociation energy of HD can be found in a brief review by Stoicheff.26 The first variational nonadiabatic calculation for HD has been performed by Bishop and Cheung.5 They used 858 basis functions, each being a product of an electronic James–Coolidge function and some radial Gaussian-type function, and obtained the nonrelativistic \(D_0 = 36405.97\) cm\(^{-1}\) with an estimated convergence error of \(0.28\) cm\(^{-1}\). Approximate relativistic (\(\sim 0.54\) cm\(^{-1}\)) and radiative (\(\sim 0.22\) cm\(^{-1}\)) corrections completed the dissociation energy to the value displayed in Table 2.

A more accurate relativistic dissociation energy of the HD molecule was first obtained by Wolniewicz27 in 1983, and later by Kolos and coworkers.28,29 In 1995 Wolniewicz has markedly improved his electronic wave functions and refined the final dissociation energy to get \(36405.787\) cm\(^{-1}\) shown in Table 2. This value differs from ours by a few thousands of a wave number in accord with the uncertainty estimated by Wolniewicz. Concerning the QED correction to the ground state \(D_0\) we mention the old but very good estimation \(-0.197\) cm\(^{-1}\) by Ladik.30 It agrees surprisingly well with the current rigorous result, see Table 1.

Last year, Stanke et al.9 performed new variational nonadiabatic calculation employing 10 000 explicitly correlated Gaussian basis functions. Their nonrelativistic total energy of \(-1.165\ 471\ 922\ 0(20)\ \text{\(E_h\)}\), when subtracted from the sum of the atomic nonadiabatic energies, eqn (34), yields \(D_0 = 36406.5105\) cm\(^{-1}\) in good agreement with our nonrelativistic subtotal value in Table 1 (the difference is \(0.0003(2)\) cm\(^{-1}\)). Their relativistic correction computed with the nonadiabatic wave function is \(-1.089\ 307\times 10^{-5}\ \text{\(E_h\)}\). Because the corresponding atomic limit (\(-x^2/4\ \text{\(E_h\)}\)) is known to a high accuracy (the leading order recoil term vanishes), the relativistic \(D_0\) can be inferred from this data as equal to \(36405.9794\) cm\(^{-1}\). We note here that now the discrepancy increases to \(0.0012(5)\) cm\(^{-1}\) in comparison with our relativistic result. If this difference were attributed to the relativistic recoil contribution, it would be almost 3 times larger than the conservative estimate of this effect discussed above.

Table 2 also collects dissociation energies determined experimentally. The first measurement of \(D_0\) for HD was performed by Herzberg and Monfils in 1960\(^{31}\) yielding \(36400.5\) cm\(^{-1}\). Motivated by a discrepancy with the famous theoretical results by Kolos and Wolniewicz,32 Herzberg repeated his experiment\(^{33,34}\) using an improved apparatus and established \(D_0 = 36406.2(4)\) cm\(^{-1}\) shown in Table 2.

Table 3 Comparison of theoretical and experimental results for the energy difference \(\Delta E\) (in cm\(^{-1}\)) between \(v = 0\) and \(v = 1\) rotationless states of HD. \(\delta\) is a difference from our result

<table>
<thead>
<tr>
<th>Source</th>
<th>(\Delta E)</th>
<th>(\delta)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This work</td>
<td>3632.1604(5)</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanke et al. (2009)(^9)</td>
<td>3632.1614(5)</td>
<td>0.0010</td>
</tr>
<tr>
<td>Wolniewicz (1995)(^{33})</td>
<td>3632.161</td>
<td></td>
</tr>
<tr>
<td>Kolos and Rychlewski (1993)(^{29})</td>
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<td></td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanke et al. (2009)(^9)</td>
<td>3632.1595(17)</td>
<td>-0.0009</td>
</tr>
<tr>
<td>Rich et al. (1982)(^{35})</td>
<td>3632.159(6)</td>
<td>-0.001</td>
</tr>
<tr>
<td>McKellar et al. (1976)(^{45})</td>
<td>3632.1529(9)</td>
<td>-0.008</td>
</tr>
</tbody>
</table>

\(\delta\) The original \(\Delta E = 3632.1802\) cm\(^{-1}\) from ref. \(9\) has been augmented by a sum of our \(x^2\) and \(x^4\) QED corrections equal to \(-0.0187\) cm\(^{-1}\). \(\delta\) 1σ uncertainty. \(\delta\) 3σ uncertainty.

Table 4 Components of theoretically predicted transition energy \(\Delta E\) between \(J = 0\) and \(J = 1\), and between \(J = 0\) and \(J = 2\) rotational levels of the ground vibrational state (\(v = 0\)) of HD. All entries in cm\(^{-1}\). \n
<table>
<thead>
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<th>Component</th>
<th>(\Delta E(0 \rightarrow 1))</th>
<th>(\Delta E(0 \rightarrow 2))</th>
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<tr>
<td>BO</td>
<td>89.270 629</td>
<td>267.196 840</td>
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<td>-0.036 086</td>
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<td>Nonadiabatic correction</td>
<td>-0.007 782(6)</td>
<td>-0.023 287(19)</td>
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<tr>
<td>(x^1) subtotal</td>
<td>89.228 709(6)</td>
<td>267.096 711(19)</td>
</tr>
<tr>
<td>(x^2) correction</td>
<td>0.010 300(2)</td>
<td>0.005 813(5)</td>
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<tr>
<td>(x^2 + x^4) subtotal</td>
<td>89.228 709(6)</td>
<td>267.096 711(19)</td>
</tr>
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<td>(x^4) correction</td>
<td>-0.000 670(4)</td>
<td>-0.000 018(9)</td>
</tr>
<tr>
<td>Total</td>
<td>89.227 933(8)</td>
<td>267.069 205(22)</td>
</tr>
<tr>
<td>Experiment(^{46,47})</td>
<td>89.227 950(5)</td>
<td>267.086(10)</td>
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Table 5  Dissociation energy (in cm\(^{-1}\)) of all 400 bound states of HD. \(v\) and \(J\) are the vibrational and rotational quantum numbers, respectively.

<table>
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<th>3</th>
<th>4</th>
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<th>8</th>
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<th>11</th>
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</table>

\(v/J\) values range from 0 to 26, with \(v\) ranging from 0 to 8 and \(J\) ranging from 0 to 36.
This value, however, is in fact an arithmetic mean of two independent measurements: 36 405.8 cm\(^{-1}\) and 36 406.6 cm\(^{-1}\), the former being very close to our value. In 1993, Eyler and Melikchi\(^{35}\) determined the dissociation threshold from the EF state and, in combination with the spectra measured by Diecke,\(^{36}\) obtained \(D_0 = 36 405.88(10)\) cm\(^{-1}\). At the same time, Balakrishnan et al.\(^{37}\) performed a delayed detection of the fluorescence spectrum of photodissociated hydrogen and arrived at \(D_0 = 36 405.83(10)\) cm\(^{-1}\). These results, although systematically larger, are in agreement within their uncertainties with current theoretical predictions. An order of magnitude more accurate measurements were reported by the Eyler group in 2004.\(^{38}\) In a three-step experiment aiming at determination of the second dissociation threshold they obtained \(D_0 = 36 405.828(16)\) cm\(^{-1}\). This result is 3\(\sigma\) away from our theoretical value. In view of an increased precision on both the experimental and theoretical side it must be stated that currently there is a discrepancy of \(ca. 0.05\) cm\(^{-1}\) in the determination of \(D_0\) for HD.

Accuracy of the present results can also be assessed by comparison of the energy difference corresponding to the lowest rotationless vibrational transition with the available literature data (see Table 3). The most accurate theoretical predictions by Wolniewicz and by Kolos and Rychlewski as well as the experimental data are in very good agreement with the present result 3632.1604(5) cm\(^{-1}\). Here, we estimated the uncertainty in the same way as for the dissociation energy (see above) i.e. assuming that the error components are proportional to corresponding corrections.

In contrast to the homonuclear isotopomers, the electric dipole transitions between the lowest rotational states of HD are allowed and the transition energy can, in principle, be measured directly. In Table 4 we present values of all significant contributions to the lowest \(J = 0 \rightarrow 1, 2\) transition energies and compare with the available experimental data – we note a 2\(\sigma\) difference between the theory and measurements.

The ionization potential (IP) of HD can be related to its dissociation energy by

\[
IP = D_0(\text{HD}) - E(H) - D_0(\text{HD}^+). \tag{52}
\]

Since the dissociation energy of HD\(^+\), as well as the total energy of the hydrogen atom, is known very accurately, we can evaluate IP with an accuracy adequate to that of \(D_0(\text{HD})\). Up-to-date values of \(E(H) = -109 678.7717\) cm\(^{-1}\) and \(D_0(\text{HD}^+) = 21 516.069 60\) cm\(^{-1}\) have been compiled by Liu et al.\(^{3}\) on the basis of current fundamental constants\(^{17}\) and calculations by Korobov.\(^{39,40}\) IP computed for HD from the above formula amounts to 124 568.4849(10) cm\(^{-1}\) with the uncertainty transferred directly from \(D_0\).

**IX. Conclusion**

The high accuracy of 0.001 cm\(^{-1}\) for the theoretically predicted dissociation energy of \(\text{H}_2\) and isotopomers has been achieved due to the recent progress made in two directions. The first one, enabled a complete treatment of the leading QED effects. In particular, the approach to effectively calculate the many electron Bethe logarithm and mean values of singular operators, like the Araki–Sucher term, has been developed.\(^{14,42}\) The second direction, indispensable for reaching this accuracy, is the nonadiabatic perturbation theory,\(^{10,11,24}\) which enables a rigorous approach to the finite nuclear mass effects beyond the adiabatic approximation. However, an accurate nonadiabatic correction to relativistic contribution still remains to be evaluated.

In comparison of theoretical predictions with recent experimental results we observe a very good agreement for dissociation energies of \(\text{H}_2\) and \(\text{D}_2\), and a small discrepancy of 0.045(16) cm\(^{-1}\) for HD. Therefore, a new measurement with an increased precision of dissociation and transition energies of HD molecule would be very desirable.

**Note added in proof**

After submitting this paper we became aware of a new measurements of HD dissociation energy [D. Sprecher, J. Liu, C. Jungen, W. Ubachs, F. Merkt, 2010, to be published]. The new value of \(D_0 = 36405.78366(36)\) cm\(^{-1}\) is in a very good agreement with our theoretical prediction.

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