Accurate theory of the hydrogen molecule

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Motivation

- benchmark calculation of relativistic and QED effects in molecular systems
- improved comparison with experimental values for H₂ levels (currently at 10⁻⁸ precision level)
- \( m_e / m_p \) from the vibrational spectrum, other constants . . .
- to discover new effects, like that in muonic versus electronic-hydrogen Lamb shift (PSI 2010), any hints ?

Collaborators

- J. Komasa (Poznań, Poland)
- B. Jeziorski and his group (Warsaw, Poland)
Determination of the dissociation energy of H$_2$ – a historical perspective

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- 1929 4.46(4) eV Richardson and Davidson present value 4.478 eV
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Challenges

- beyond Born-Oppenheimer: combined finite nuclear mass and (relativistic) QED corrections to rovibrational energies, shielding constant, . . .

- higher order QED effects $\sim \alpha^4 \text{Ry}$

- extension of the computational technique to an arbitrary light molecule
Atomic or molecular energy

\[ E(\alpha, \beta) = E_0 + \alpha^2 E_{\text{REL}} + \alpha^3 E_{\text{QED}} + \alpha^4 E_{\text{HQED}} + \ldots \]

\[ + \beta E_{\text{AD}} + \alpha^2 \beta E_{\text{rec}}^{\text{REL}} + \alpha^3 \beta E_{\text{rec}}^{\text{QED}} + \ldots \]

\[ + \beta^2 E_{\text{NA}} + \ldots \]

\[ E_0 \] – Born-Oppenheimer energy

\[ E_{\text{AD}} \] – adiabatic correction

\[ E_{\text{NA}} \] – nonadiabatic correction

\[ \alpha^2 E_{\text{REL}} \] – relativistic correction

\[ \alpha^3 E_{\text{QED}} \] – leading radiative (QED) correction

\[ \alpha^4 E_{\text{HQED}} \] – higher order QED correction

\[ \alpha \approx 1/137 \] – fine structure constant, \( \beta = m_e/\mu_n \approx 10^{-3} \) electron-nuclear mass ratio
Atomic or molecular energy

\( \alpha \approx 1/137 \) – fine structure constant, \( \beta = \frac{m_e}{\mu_n} \sim 10^{-3} \) electron-nuclear mass ratio

\[
E(\alpha, \beta) = E_0 + \alpha^2 E_{\text{REL}} + \alpha^3 E_{\text{QED}} + \alpha^4 E_{\text{HQED}} + \ldots
\]

- \( E_0 \) – Born-Oppenheimer energy
- \( E_{\text{AD}} \) – adiabatic correction
- \( E_{\text{NA}} \) – nonadiabatic correction
- \( \alpha^2 E_{\text{REL}} \) – relativistic correction
- \( \alpha^3 E_{\text{QED}} \) – leading radiative (QED) correction
- \( \alpha^4 E_{\text{HQED}} \) – higher order QED correction
Nonrelativistic Schrödinger equation

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

\[ H = H_{\text{el}} + H_n \]

\[ H_{\text{el}} = - \sum_a \frac{\nabla^2_a}{2 m_e} + V \]

\[ H_n = - \frac{\nabla^2_R}{2 \mu_n} - \frac{\nabla^2_{\text{el}}}{2 \mu_n} - \left( \frac{1}{M_B} - \frac{1}{M_A} \right) \vec{\nabla}_R \cdot \vec{\nabla}_{\text{el}} \]

\[ \vec{R} = \vec{R}_A - \vec{R}_B \]

\[ \frac{1}{\mu_n} = \frac{1}{M_B} + \frac{1}{M_A} \]

\[ \vec{\nabla}_{\text{el}} \equiv \frac{1}{2} \sum_a \vec{\nabla}_a \]

Diatomuc molecules, coordinate system origin at the bond midpoint
Adiabatic approximation

perturbative expansion

\[ \phi = \phi_a + \delta \phi_{na} \]
\[ E = E_a + \delta E_{na} \]

adiabatic assumption

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

\[ [H_{el} - \mathcal{E}_{el}(\vec{R})] |\phi_{el}\rangle = 0 \]

nuclear equation

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

\[ \mathcal{E}_a(R) = \langle \phi_{el}|H_n|\phi_{el}\rangle_{el} \]

Nonadiabatic corrections from NAPT
## Comparison with direct variational calculations

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<tr>
<th>Molecule</th>
<th>Method</th>
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<td>NAPT$^2$</td>
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$^1$M. Stanke, D. Kędziera, S. Bubin, M. Molski, L. Adamowicz, *JCP* **128**, 114313 (2008);

$^2$K. Pachucki, J. Komasa, *JCP* **130**, 164113 (2009);

$^3$Piszczatowski, Lach, Przybytek, Komasa, Pachucki, Jeziorski, *JCTC* **5**, 3039 (2009);


Expectation value of the Breit-Pauli Hamiltonian

\[ E_{\text{REL}} = \sum_{a} \left[ -\frac{1}{8} \langle \phi_{el} | p_{a}^{4} | \phi_{el} \rangle + \sum_{l} \frac{Z_{l} \pi}{2} \langle \phi_{el} | \delta(\vec{r}_{al}) | \phi_{el} \rangle \right] \\
+ \sum_{a > b} \left[ \pi \langle \phi_{el} | \delta(\vec{r}_{ab}) | \phi_{el} \rangle + \frac{1}{2} \left\langle \phi_{el} \left| \vec{p}_{a} \frac{1}{r_{ab}} \vec{p}_{b} + \vec{p}_{a} \cdot \vec{r}_{ab} \frac{1}{r_{ab}^{3}} \vec{r}_{ab} \cdot \vec{p}_{b} \right| \phi_{el} \right\rangle \right] \\
+ \frac{2 \pi}{3} \sum_{l} \frac{Z_{l} r_{\text{ch}}^{2}(l)}{\chi_{e}^{2}} \left\langle \phi_{el} \left| \sum_{a} \delta(\vec{r}_{al}) \right| \phi_{el} \right\rangle \]
Leading radiative correction

\[ E(\alpha) = (E_0 + E_{AD} + E_{NA}) + \alpha^2 E_{REL} + \alpha^3 E_{QED} + \alpha^4 E_{HQED} \]

\[ E_{QED} = \sum_{a>b} \left\{ \left[ \frac{164}{15} + \frac{14}{3} \ln \alpha \right] \langle \phi_{el} | \delta(\vec{r}_{ab}) | \phi_{el} \rangle \right. \\
- \frac{14}{3} \left\langle \phi_{el} \left| \frac{1}{4\pi} P \left( \frac{1}{r_{ab}^3} \right) \right| \phi_{el} \right\rangle \right\} \\
+ \sum_{a} \left[ \frac{19}{30} + \ln(\alpha^{-2}) - \ln k_0 \right] \sum_{l} \frac{4Z_l}{3} \left\langle \phi_{el} | \delta(\vec{r}_{al}) | \phi_{el} \right\rangle \]

\[ \ln k_0 = \frac{\langle \phi_{el} | \vec{\nabla} (H_0 - E_0) \frac{\ln[2(H_0 - E_0)]}{2} \vec{\nabla} | \phi_{el} \rangle}{\langle \phi_{el} | \vec{\nabla} (H_0 - E_0) \vec{\nabla} | \phi_{el} \rangle} \]
Higher order QED corrections

\[ E(\alpha) = (E_0 + E_{AD} + E_{NA}) + \alpha^2 E_{REL} + \alpha^3 E_{QED} + \alpha^4 E_{HQED} \]

- very difficult to calculate, known only for hydrogen and helium \(^6\)
- approximate formula

\[ E_{HQED} \approx \sum_l 4 \pi Z_l^2 \left( \frac{139}{128} + \frac{5}{192} - \frac{\ln 2}{2} \right) \sum_a \langle \phi_{el} | \delta(\vec{r}_a) | \phi_{el} \rangle \]

\(^6\)K. Pachucki, *Phys. Rev. A* 74, 062510 (2006);
Variational approach in the exponential basis

Wave function expanded in terms of exponential functions

\[ \phi = \sum c e^{-\alpha r_{1A} - \beta r_{1B} - \gamma r_{2A} - \delta r_{2B} r_{1A}^i r_{1B}^{-j} r_{2A}^k r_{2B}^l r_{12}^n} \]

with

\[ i + j + k + n + l \leq \Omega \]

Matrix elements with this basis functions have been investigated for many years, and are considered to be very difficult in the accurate evaluation.
master integral

\[ f(r) = \int \frac{d^3 r_1}{4 \pi} \int \frac{d^3 r_2}{4 \pi} \frac{e^{-u_3 r_{1A}}}{r_{1A}} \frac{e^{-u_2 r_{1B}}}{r_{1B}} \frac{e^{-w_2 r_{2A}}}{r_{2A}} \frac{e^{-w_3 r_{2B}}}{r_{2B}} \frac{r}{r_{12}} \]

others by recurrence relations

\[ f_n(i, j, k, l; r) = \int \frac{d^3 r_1}{4 \pi} \int \frac{d^3 r_2}{4 \pi} \frac{e^{-u_3 r_{1A}}}{r_{1A}^{1-i}} \frac{e^{-u_2 r_{1B}}}{r_{1B}^{1-j}} \frac{e^{-w_2 r_{2A}}}{r_{2A}^{1-k}} \frac{e^{-w_3 r_{2B}}}{r_{2B}^{1-l}} \frac{r}{r_{12}^{1-n}} \]

→ analytic solution for arbitrary powers
Special case: symmetric

\[
f(n_1, n_2, n_3, n_4, n_5; r) = \int \frac{d^3 r_1}{4 \pi} \int \frac{d^3 r_2}{4 \pi} \frac{e^{-u r_1 A}}{r_1 A} \frac{e^{-u r_1 B}}{r_1 B} \frac{e^{-w r_2 A}}{r_2 A} \frac{e^{-w r_2 B}}{r_2 B} \frac{r}{r_{12}^{1-n_1}}
\]

\[
\begin{align*}
(r_1 A - r_1 B)^{n_2} (r_2 A - r_2 B)^{n_3} (r_1 A + r_1 B)^{n_4} (r_2 A + r_2 B)^{n_5}
\end{align*}
\]

\[
f(0, 0, 0, 0, 0; r) = \frac{1}{4 u w} \left[ e^{r (u+w)} \text{Ei}(-2 r (u+w)) + e^{-r (u+w)} \left( \gamma + \ln \frac{2 ruw}{u+w} \right) \\
- e^{r (u-w)} \text{Ei}(-2 r u) - e^{r (w-u)} \text{Ei}(-2 r w) \right]
\]

\[
f(2, 0, 0, 0, 0; r) = \frac{(u^2 + w^2)}{6 u^2 w^2} f(0, 0, 0, 0, 0; r) + \frac{e^{-r (u+w)} r^2}{12 uw} \]

\[
+ \frac{r}{24 u^2 w^2} \left[ (u + w) e^{-r (u+w)} - (u - w) e^{r (u-w)} \text{Ei}(-2 r u) \\
- (w - u) e^{r (w-u)} \text{Ei}(-2 r w) - (u + w) e^{r (u+w)} \text{Ei}(-2 r (u + w)) \\
+ (u + w) e^{-r (u+w)} \left( \gamma + \ln \frac{2 ruw}{u+w} \right) \right]
\]
Born-Oppenheimer potential

\[ E(1.4011) = -1.1744759314002167(3) \]
Dissociation energy of all rovibrational states of H₂, HD and D₂

Rovibrational levels of H₂ (in cm⁻¹)

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<th>v_3</th>
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Rovibrational levels of HD (in cm⁻¹)

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</tr>
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<td>3</td>
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<td>0</td>
<td>1744.62</td>
</tr>
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</table>

Rovibrational levels of D₂ (in cm⁻¹)

<table>
<thead>
<tr>
<th>J</th>
<th>v_1</th>
<th>v_2</th>
<th>v_3</th>
<th>Energy (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1851.62</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1865.62</td>
</tr>
</tbody>
</table>
# Dissociation energy of H₂ and D₂ in cm⁻¹

<table>
<thead>
<tr>
<th></th>
<th>H₂</th>
<th>D₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha^0 )</td>
<td>Nonrelativistic</td>
<td>36118.7978(2)</td>
</tr>
<tr>
<td>( \alpha^2 )</td>
<td>Mass-velocity</td>
<td>4.4273(2)</td>
</tr>
<tr>
<td></td>
<td>1-el. Darwin</td>
<td>-4.9082(2)</td>
</tr>
<tr>
<td></td>
<td>2-el. Darwin</td>
<td>-0.5932(1)</td>
</tr>
<tr>
<td></td>
<td>Breit</td>
<td>0.5422(1)</td>
</tr>
<tr>
<td></td>
<td>Total ( \alpha^2 )</td>
<td>-0.5319(3)</td>
</tr>
<tr>
<td>( \alpha^2 )</td>
<td>( m_e/m_p ) Estimate</td>
<td>0.0000(4)</td>
</tr>
<tr>
<td>( \alpha^3 )</td>
<td>1-el. Lamb shift</td>
<td>-0.2241(1)</td>
</tr>
<tr>
<td></td>
<td>2-el. Lamb shift</td>
<td>0.0166(1)</td>
</tr>
<tr>
<td></td>
<td>Araki-Sucher</td>
<td>0.0127(1)</td>
</tr>
<tr>
<td></td>
<td>Total ( \alpha^3 )</td>
<td>-0.1948(2)</td>
</tr>
<tr>
<td>( \alpha^3 )</td>
<td>( m_e/m_p ) Estimate</td>
<td>0.0000(2)</td>
</tr>
<tr>
<td>( \alpha^4 )</td>
<td>One-loop term</td>
<td>-0.0016(8)</td>
</tr>
<tr>
<td>Total theory</td>
<td></td>
<td>36118.0695(10)</td>
</tr>
<tr>
<td>Expt. 2004</td>
<td>Eyler</td>
<td>36118.062(10)</td>
</tr>
<tr>
<td>Expt. 2010</td>
<td>Merkt&amp;Ubachs</td>
<td>36118.0696(4)</td>
</tr>
</tbody>
</table>
# Dissociation energy of H$_2$ and D$_2$ in cm$^{-1}$

<table>
<thead>
<tr>
<th></th>
<th>H$_2$</th>
<th>D$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha^0$ Nonrelativistic</td>
<td>36118.7978(2)</td>
<td>36749.0910(2)</td>
</tr>
<tr>
<td>$\alpha^2$ Mass-velocity</td>
<td>4.4273(2)</td>
<td>4.5125(2)</td>
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<tr>
<td>1-el. Darwin</td>
<td>-4.9082(2)</td>
<td>-4.9873(2)</td>
</tr>
<tr>
<td>2-el. Darwin</td>
<td>-0.5932(1)</td>
<td>-0.5993(1)</td>
</tr>
<tr>
<td>Breit</td>
<td>0.5422(1)</td>
<td>0.5465(1)</td>
</tr>
<tr>
<td>Total $\alpha^2$</td>
<td>-0.5319(3)</td>
<td>-0.5276(3)</td>
</tr>
<tr>
<td>$\alpha^2 m_e/m_p$ Estimate</td>
<td>0.0000(4)</td>
<td>0.0000(2)</td>
</tr>
<tr>
<td>$\alpha^3$ 1-el. Lamb shift</td>
<td>-0.2241(1)</td>
<td>-0.2278(1)</td>
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<tr>
<td>2-el. Lamb shift</td>
<td>0.0166(1)</td>
<td>0.0167(1)</td>
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<tr>
<td>Araki-Sucher</td>
<td>0.0127(1)</td>
<td>0.0128(1)</td>
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<tr>
<td>Total $\alpha^3$</td>
<td>-0.1948(2)</td>
<td>-0.1983(2)</td>
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<tr>
<td>$\alpha^3 m_e/m_p$ Estimate</td>
<td>0.0000(2)</td>
<td>0.0000(1)</td>
</tr>
<tr>
<td>$\alpha^4$ One-loop term</td>
<td>-0.0016(8)</td>
<td>-0.0016(8)</td>
</tr>
<tr>
<td>Total theory</td>
<td>36118.0695(10)</td>
<td>36748.3633(9)</td>
</tr>
<tr>
<td>Expt. 2004 Eyler</td>
<td>36118.062(10)</td>
<td>36748.343(10)</td>
</tr>
<tr>
<td>Expt. 2010 Merkt&amp;Ubachs</td>
<td>36118.0696(4)</td>
<td>36748.3629(6)</td>
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## Excitation energies of H_2 and D_2

<table>
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<tr>
<th></th>
<th>J = 0 → 1</th>
<th>ν = 0 → 1</th>
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<tbody>
<tr>
<td>α^0</td>
<td></td>
<td></td>
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<tr>
<td>Born-Oppenheimer</td>
<td>118.55558(2)</td>
<td>4163.4035(1)</td>
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<tr>
<td>Adiabatic</td>
<td>-0.06365(4)</td>
<td>-1.4029(1)</td>
</tr>
<tr>
<td>Nonadiabatic</td>
<td>-0.00667(8)</td>
<td>-0.8365(2)</td>
</tr>
<tr>
<td>Total α^0</td>
<td>118.48526(9)</td>
<td>4161.1641(2)</td>
</tr>
<tr>
<td>α^2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass-velocity</td>
<td>0.02713(4)</td>
<td>0.5347(2)</td>
</tr>
<tr>
<td>1-el. Darwin</td>
<td>-0.02383(4)</td>
<td>-0.4994(2)</td>
</tr>
<tr>
<td>2-el. Darwin</td>
<td>-0.00160(2)</td>
<td>-0.0391(1)</td>
</tr>
<tr>
<td>Breit</td>
<td>0.00088(2)</td>
<td>0.0279(1)</td>
</tr>
<tr>
<td>Total α^2</td>
<td>0.00258(6)</td>
<td>0.0235(3)</td>
</tr>
<tr>
<td>α^3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-el. Lamb shift</td>
<td>-0.00109(2)</td>
<td>-0.0231(1)</td>
</tr>
<tr>
<td>2-el. Lamb shift</td>
<td>0.00004(1)</td>
<td>0.0011(1)</td>
</tr>
<tr>
<td>Araki-Sucher</td>
<td>0.00002(1)</td>
<td>0.0007(1)</td>
</tr>
<tr>
<td>Total α^3</td>
<td>-0.00103(3)</td>
<td>-0.0213(2)</td>
</tr>
<tr>
<td>α^4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>One-loop term</td>
<td>-0.00001(1)</td>
<td>-0.0002(2)</td>
</tr>
<tr>
<td><strong>Total theory</strong></td>
<td><strong>118.48680(11)</strong></td>
<td><strong>4161.1661(5)</strong></td>
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<tr>
<td><strong>Experiment</strong></td>
<td><strong>118.48684(10)</strong></td>
<td><strong>4161.1660(3)</strong></td>
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Comparison of theoretical and experimental results for $D_0$ in cm$^{-1}$ of HD

<table>
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<tr>
<th>Component</th>
<th>$D_0$</th>
<th>$\delta$</th>
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<tbody>
<tr>
<td>This work</td>
<td>36 405.7828(10)</td>
<td></td>
</tr>
<tr>
<td>Theory</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stanke (2009)</td>
<td>36 405.7814$^a$</td>
<td>0.0014</td>
</tr>
<tr>
<td>Wolniewicz (1995)</td>
<td>36 405.787</td>
<td>0.004</td>
</tr>
<tr>
<td>Kołos and Rychlewski (1993)</td>
<td>36 405.763</td>
<td>0.020</td>
</tr>
<tr>
<td>Kołos, Szalewicz, Monkhorst (1986)</td>
<td>36 405.784</td>
<td>0.001</td>
</tr>
<tr>
<td>Wolniewicz (1983)</td>
<td>36 405.73</td>
<td>0.05</td>
</tr>
<tr>
<td>Bishop and Cheung (1978)</td>
<td>36 405.49</td>
<td>-0.29</td>
</tr>
<tr>
<td>Experiment</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Merkt &amp; Ubachs (2010)</td>
<td>36 405.78366(36)</td>
<td>0.0009</td>
</tr>
<tr>
<td>Zhang (2004)</td>
<td>36 405.828(16)</td>
<td>0.045</td>
</tr>
<tr>
<td>Balakrishnan (1993)</td>
<td>36 405.83(10)</td>
<td>0.05</td>
</tr>
<tr>
<td>Eyler and Melikechi (1993)</td>
<td>36 405.88(10)</td>
<td>0.10</td>
</tr>
<tr>
<td>Herzberg (1970)</td>
<td>36 406.2(4)</td>
<td>0.4</td>
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</table>

$^a$ Their $D_0 = 36 405.9794$ cm$^{-1}$ has been augmented by a sum of our $\alpha^3$ and $\alpha^4$ QED corrections equal to $-0.1980$ cm$^{-1}$.
## ΔE between rotational levels of the ground vibrational state (ν = 0) of HD, in cm⁻¹

<table>
<thead>
<tr>
<th>Component</th>
<th>ΔE(0 → 1)</th>
<th>ΔE(0 → 2)</th>
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</thead>
<tbody>
<tr>
<td>BO</td>
<td>89.270 629</td>
<td>267.196 840</td>
</tr>
<tr>
<td>Adiabatic correction</td>
<td>−0.036 086</td>
<td>−0.107 842</td>
</tr>
<tr>
<td>Nonadiabatic correction</td>
<td>−0.007 782(6)</td>
<td>−0.023 287(19)</td>
</tr>
<tr>
<td>α⁰ subtotal</td>
<td>89.226 761(6)</td>
<td>267.065 711(19)</td>
</tr>
<tr>
<td>α² correction</td>
<td>0.001 948(2)</td>
<td>0.005 813(5)</td>
</tr>
<tr>
<td>α⁰+α² subtotal</td>
<td>89.228 709(6)</td>
<td>267.071 524(20)</td>
</tr>
<tr>
<td>α³ correction</td>
<td>−0.000 771(1)</td>
<td>−0.002 303(2)</td>
</tr>
<tr>
<td>α⁴ correction</td>
<td>−0.000 007(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>Evenson (1988)/Stoicheff (1957)</td>
<td>89.227 950(5)</td>
<td>267.086(10)</td>
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</table>
\( \Delta E \) between rotational levels of the ground vibrational state \((v = 0)\) of HD, in cm\(^{-1}\)

<table>
<thead>
<tr>
<th>Component</th>
<th>( \Delta E(0 \to 1) )</th>
<th>( \Delta E(0 \to 2) )</th>
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</thead>
<tbody>
<tr>
<td>BO</td>
<td>89.270 629</td>
<td>267.196 840</td>
</tr>
<tr>
<td>Adiabatic correction</td>
<td>−0.036 086</td>
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<tr>
<td>Nonadiabatic correction</td>
<td>−0.007 782(6)</td>
<td>−0.023 287(19)</td>
</tr>
<tr>
<td>( \alpha^0 ) subtotal</td>
<td>89.226 761(6)</td>
<td>267.065 711(19)</td>
</tr>
<tr>
<td>( \alpha^2 ) correction</td>
<td>0.001 948(2)</td>
<td>0.005 813(5)</td>
</tr>
<tr>
<td>( \alpha^0 + \alpha^2 ) subtotal</td>
<td>89.228 709(6)</td>
<td>267.071 524(20)</td>
</tr>
<tr>
<td>( \alpha^3 ) correction</td>
<td>−0.000 771(1)</td>
<td>−0.002 303(2)</td>
</tr>
<tr>
<td>( \alpha^4 ) correction</td>
<td>−0.000 007(4)</td>
<td>−0.000 018(9)</td>
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<tr>
<td>Total</td>
<td>89.227 933(8)</td>
<td>267.069 205(22)</td>
</tr>
<tr>
<td>Evenson (1988)/Stoicheff (1957)</td>
<td>89.227 950(5)</td>
<td>267.086(10)</td>
</tr>
<tr>
<td>Drouin (2010)</td>
<td>89.227 9326(3)</td>
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</tr>
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analytic formulae for two-center Slater integrals

highest accuracy ever achieved for BO potential of H$_2$

very good convergence with exponential basis set

higher order QED corrections can be evaluated as accurately as for H$_2^+$

more problematic are the finite nuclear mass corrections

possible generalizations to the 3- and more electrons molecule