# Quantum Electrodynamics Effects in Rovibrational Spectra of Molecular Hydrogen

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Ⓢ Supporting Information

**ABSTRACT:** The dissociation energies from all rovibrational levels of $H_2$ and $D_2$ in the ground electronic state are calculated with high accuracy by including relativistic and quantum electrodynamics (QED) effects in the nonadiabatic treatment of the nuclear motion. For $D_2$, the obtained energies have theoretical uncertainties of 0.001 cm$^{-1}$. For $H_2$, similar uncertainties are for the lowest levels, while for the higher ones the uncertainty increases to 0.005 cm$^{-1}$. Very good agreement with recent high-resolution measurements of the rotational $v = 0$ levels of $H_2$, including states with large angular momentum $J$, is achieved. This agreement would not have been possible without accurate evaluation of the relativistic and QED contributions and may be viewed as the first observation of the QED effects, mainly the electron self-energy, in a molecular spectrum. For several electric quadrupole transitions, we still observe certain disagreement with experimental results, which remains to be explained.

## 1. INTRODUCTION

Due to its simplicity, the hydrogen molecule and its isotopomers $D_2$ and HD are natural benchmark systems for testing various computational and experimental approaches in molecular spectroscopy. The measurements of their rovibrational levels have reached such a precision level[1−4] that not only the nonadiabatic and the leading relativistic effects but also quantum electrodynamics (QED) and possibly finite nuclear size corrections become important. In this work, we exploit recent theoretical progress in calculating the spectra of $H_2$ and $D_2$ using explicitly correlated basis sets built of Gaussian or exponential functions. For the latter, exact analytic formulas have recently been derived,[5] making possible the calculation of the Born−Oppenheimer potential with an uncertainty smaller than $10^{-9}$ cm$^{-1}$. The finite nuclear mass effects are calculated using nonadiabatic perturbation theory (NAPT).[6,7] In this approach, leading nonadiabatic corrections are obtained by solving a suitable modification of the radial Schrödinger equation for the nuclear motion. The advantage of this procedure is that three universal nonadiabatic potentials entering this equation are sufficient to obtain all rovibrational levels supported by a given electronic state. At the precision level adequate for the present purposes, the relativistic, QED, and finite nuclear size effects can be taken into account at the adiabatic level of theory and included by means of appropriate corrections to the Born−Oppenheimer potential. These corrections are expectation values of the Breit−Pauli Hamiltonian,[8] or effective QED operators,[9] computed with the clamped nuclei nonrelativistic electronic wave function. Our approach is based on the expansion of energy levels in powers of fine structure constant $\alpha$,[10,11] which was originally developed for hydrogenic systems and applied in highly accurate calculations for light atoms.[12−15]

## 2. HISTORICAL PERSPECTIVE

A meaningful confrontation of theoretically predicted rovibrational levels with high-resolution spectroscopy measurements became possible in 1983 with the appearance of the pioneering work of Wolniewicz,[16] who accurately computed the nonadiabatic corrections to all vibrational levels of $H_2$, HD, and $D_2$. For the $H_2$ molecule, Wolniewicz observed a significant disagreement of up to 0.7 cm$^{-1}$ with the experimental vibrational excitation energies available at that time.[17] In a subsequent development, Kolos et al.[18] recomputed the Born−Oppenheimer potential for $H_2$, obtaining the adiabatic levels 0.1−0.2 cm$^{-1}$ below the Wolniewicz values. Using the nonadiabatic corrections from the Wolniewicz work, the authors of ref 18 obtained improved agreement (with errors up to 0.2−0.3 cm$^{-1}$) when compared with a more recent measurement of Dabrowski.[19]

The works of Wolniewicz[16] and of Kolos et al.[18] were based on the relativistic corrections computed in 1964[20] using a rather small basis (of James and Coolidge type[21]) and only for internuclear distances $R \leq 3.7$ bohr. To eliminate this source of uncertainty, Wolniewicz[22] recomputed in 1993 the relativistic corrections for a wide range of distances employing a large, asymptotically correct basis set introduced in 1966 by Kolos and Wolniewicz.[23] To obtain the nonadiabatic corrections, Wolniewicz used an *ab initio* based scaling and extrapolation procedure proposed by Schwartz and LeRoy,[24] which he believed to be more reliable (except for $v = J = 0$) than his *ab initio* data of 1983.[16] This work led to some improvement in agreement with the experimental vibrational spectrum

of Dabrowski,[19] as compared with the 1986 work of Kolos et al.[18]

As the method of Schwartz and LeRoy[24] had not been performing very satisfactorily in some applications, especially in the cases of HD and HT,[25] in 1995 Wolniewicz[26] recomputed the nonadiabatic corrections obtaining significantly more accurate values for higher vibrational levels. This resulted in further improvement of the agreement with the vibrational quanta of ref 19. It is difficult to say how significant this improvement was, since the disagreement with the experimental results of Dabrowski[19] was on the last digit reported by her and the corresponding experimental uncertainty is not clear.

According to Wolniewicz,[26] the main source of uncertainty of his results is the QED corrections, which he evaluated only approximately. These corrections are accurately taken into account in the present calculations, with all $\alpha^3$ and the leading $\alpha^4$ terms included ($\alpha$ is the fine structure constant). Results for the ground rovibrational state (i.e., for the dissociation energy) of $H_2$ and $D_2$ have already been presented by us in ref 27 and for HD in ref 28. Very recently, Salumbides et al.[29] reported highly accurate experimental values of the rotational energies of $\nu = 0$ levels of $H_2$. The uncertainty of the majority of these levels ranges from 0.0001 cm$^{-1}$ up to 0.005 cm$^{-1}$. Such an accuracy, in connection with our calculations, is sufficient to determine the magnitude of QED effects directly from the measurements. It should be noted that QED corrections have also been treated for more complex systems, such as the water molecule,[30] but using an approximate one-electron approach; thus not all of the $\alpha^3$ terms were taken into account. However, for such systems, the nonrelativistic treatment of the spectrum is still not accurate enough to see QED effects in a head-on comparison between theory and experiment.[31]

## 3. THE NONADIABATIC SCHRÖDINGER EQUATION

The nonrelativistic Schrödinger equation is solved using the NAPT approach.[6,7] For electronic states of $\Sigma$ symmetry, the zeroth-order approximation to the total wave function can be assumed to be a product of the electronic $\phi_{el}$ and nuclear $\chi$ functions (atomic units will be used throughout):

$$\phi_a(\vec{r}, \vec{R}) = \phi_{el}(\vec{r}; \vec{R})\,\chi(\vec{R}) \tag{1}$$

The electronic wave function $\phi_{el}$ satisfies the clamped nuclei Schrödinger equation:

$$[H_{el} - \mathscr{E}_{el}(R)]\phi_{el} = 0 \tag{2}$$

where $H_{el}$ is the electronic Hamiltonian, and thus parametrically depends on the internuclear distance $R$. The function $\chi$ satisfies the nuclear Schrödinger equation

$$\left[-\frac{\nabla_R^2}{2\mu_n} + \mathscr{E}_{el}(R) + \mathscr{E}_a(R)\right]\chi(\vec{R}) = E_a\chi(\vec{R}) \tag{3}$$

with $\mu_n$ being the nuclear reduced mass, and the adiabatic correction $\mathscr{E}_a(R)$ is given by the electronic matrix element

$$\mathscr{E}_a(R) = \langle\phi_{el}|H_n|\phi_{el}\rangle_{el} \tag{4}$$

of the nuclear part $H_n = H - H_{el}$ of the total Hamiltonian $H$ (the brackets $\langle\cdots\rangle_{el}$ denote integration over the electronic coordinates only). For specified angular momentum $J$, the nuclear

equation becomes

$$\left[-\frac{1}{R^2}\frac{\partial}{\partial R}\frac{R^2}{2\mu_n}\frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_n R^2} + \mathscr{E}_a(R) + \mathscr{E}_{el}(R)\right]\chi_J(R)$$
$$= E_a\chi_J(R) \tag{5}$$

Using NAPT,[6,7] all of the finite nuclear mass corrections are obtained perturbatively in progressive powers of the electron–nuclear mass ratio. Up to the order $\mathcal{O}(\mu_n^{-2})$, they can all be included in the following radial equation as an $R$-dependent modification of the effective nuclear reduced mass and of the interaction potential:

$$\left[-\frac{1}{R^2}\frac{\partial}{\partial R}\frac{R^2}{2\mu_{\|}(R)}\frac{\partial}{\partial R} + \frac{J(J+1)}{2\mu_{\perp}(R)R^2} + \mathscr{Y}(R)\right]\tilde{\chi}_J(R)$$
$$= E\tilde{\chi}_J(R) \tag{6}$$

where

$$\mathscr{Y}(R) = \mathscr{E}_{el}(R) + \mathscr{E}_a(R) + \delta\mathscr{E}_{na}(R) \tag{7}$$

The modifications of the effective nuclear reduced mass are of the form

$$\frac{1}{2\mu_{\|}(R)} \equiv \frac{1}{2\mu_n}$$
$$+ \frac{1}{\mu_n^2}\left\langle\vec{n}\cdot\vec{\nabla}_R\phi_{el}\left|\frac{1}{(\mathscr{E}_{el} - H_{el})'}\right|\vec{n}\cdot\vec{\nabla}_R\phi_{el}\right\rangle_{el} \tag{8}$$

and

$$\frac{1}{2\mu_{\perp}(R)} \equiv \frac{1}{2\mu_n}$$
$$+ \frac{1}{\mu_n^2}\sum_{i,j}\frac{(\delta^{ij} - n^i n^j)}{2}\left\langle\nabla_R^i\phi_{el}\left|\frac{1}{\mathscr{E}_{el} - H_{el}}\right|\nabla_R^j\phi_{el}\right\rangle_{el} \tag{9}$$

with $\vec{n} = \vec{R}/R$ and the *prime* in the resolvent indicating the orthogonalization to $\phi_{el}$. The concept of the variable nuclear reduced mass has been present in the literature for a long time now,[32−35] and NAPT supplies explicit formulas for their numerical evaluation. The nonadiabatic correction $\delta\mathscr{E}_{na}(R)$ to the interaction potential can also be expressed in terms of the second-order electronic matrix elements. Since the corresponding formula is rather complicated, we refer the reader to refs 6 and 7 for its detailed form. The main advantage of the presented approach is that a single radial equation (eq 6) gives quite accurately all (nonrelativistic) rovibrational states of a diatomic molecule. In the present implementation of NAPT, the computational precision is limited by neglected $\mathcal{O}(\mu_n^{-5/2})$ corrections, which for the dissociation energy of the lowest rovibrational state are estimated to amount about 0.0001 cm$^{-1}$. Other important corrections are considered in the following section.

## 4. RELATIVISTIC AND QED CORRECTIONS

When computed using the adiabatic wave function of eq 1, the leading-order relativistic, QED, and finite nuclear size corrections enter only through an effective potential $\mathcal{Y}(R)$, namely

$$\mathcal{Y}(R) = \mathcal{E}_{el}(R) + \mathcal{E}_a(R) + \delta\mathcal{E}_{na}(R) + \mathcal{E}^{(2)}(R)$$
$$+ \mathcal{E}^{(3)}(R) + \mathcal{E}^{(4)}(R) + \mathcal{E}_{fs}(R)$$

(10)

The relativistic correction $\mathcal{E}^{(2)}(R)$ is the electronic expectation value of the Breit−Pauli Hamiltonian,[8] which for a $\Sigma$ state of a many-electron molecule is

$$\mathcal{E}^{(2)}(R) = \alpha^2 \left\langle \phi_{el} \left| -\frac{1}{8}\sum_a p_a^4 + \frac{\pi}{2}\sum_{a,A} Z_A \delta(\vec{r}_{aA}) + \pi\sum_{a<b}\delta(\vec{r}_{ab}) \right. \right.$$
$$\left. \left. -\frac{1}{2}\sum_{a<b}\left( \vec{p}_a \frac{1}{r_{ab}} \vec{p}_b + \vec{p}_a \cdot \vec{r}_{ab} \frac{1}{r_{ab}^3} \vec{r}_{ab} \cdot \vec{p}_b \right) \right| \phi_{el} \right\rangle_{el}$$

(11)

where the indices $a$ and $A$ correspond to electrons and nuclei, respectively.

The leading QED correction for a $\Sigma$ state is

$$\mathcal{E}^{(3)}(R) = \alpha^3 \sum_{a<b}\left\{ \left[\frac{164}{15} + \frac{14}{3}\ln\alpha\right]\langle\phi_{el}|\delta(\vec{r}_{ab})|\phi_{el}\rangle_{el} \right.$$

$$\left. -\frac{7}{6\pi}\left\langle\phi_{el}\left|\frac{1}{r_{ab}^3}\right|\phi_{el}\right\rangle_{el}\right\}$$

$$+ \alpha^3 \sum_{a,A}\left[\frac{19}{30} - 2\ln\alpha - \ln k_0(R)\right]\frac{4Z_A}{3}\langle\phi_{el}|\delta(\vec{r}_{aA})|\phi_{el}\rangle_{el}$$

(12)

The matrix element of $1/r_{ab}^3$ requires subtraction of a divergence at $r_{ab} = 0$; for details, see ref 9. In the adiabatic approximation, the $R$-dependent Bethe logarithm $\ln k_0(R)$ is defined by[27]

$$\ln k_0(R) = \frac{\langle\phi_{el}|\sum_a \vec{p}_a (H_{el} - \mathcal{E}_{el})\ln[2(H_{el} - \mathcal{E}_{el})]\sum_b \vec{p}_b|\phi_{el}\rangle}{\langle\phi_{el}|\sum_a \vec{p}_a (H_{el} - E_{el})\sum_b \vec{p}_b|\phi_{el}\rangle}$$

(13)

The $\alpha^4$ and higher-order QED corrections[36,37] are in general not known for molecules. One can however approximate them by the numerically dominating one-loop self-energy and vacuum polarization corrections known from the hydrogenic Lamb shift:[36]

$$\mathcal{E}^{(4)}_{one\text{-}loop}(R) = \pi\alpha^4\left(\frac{427}{96} - \ln 4\right)\sum_{a,A} Z_A\langle\phi_{el}|\delta(\vec{r}_{aA})|\phi_{el}\rangle_{el}$$

(14)

On the basis of the atomic calculations,[36,37] we conservatively estimate that this formula approximates the accurate value of $\mathcal{E}^{(4)}$ with an error of at most 50%.

The finite nuclear size correction $\mathcal{E}_{fs}(R)$ is given, to a very good approximation, by the root-mean-square nuclear charge radius $r_{ch}$:

$$\mathcal{E}_{fs}(R) = \frac{2\pi}{3}\alpha^2 \sum_{a,A} Z_A \frac{r_{ch}^2(A)}{\lambda_C^2}\langle\phi_{el}|\delta(\vec{r}_{aA})|\phi_{el}\rangle_{el}$$

(15)

where $\lambda_C = 386.15926459$ fm is the Compton wavelength over $2\pi$ ($r_{ch}(H) = 0.84184(67)$ fm and $r_{ch}(D) = 2.1402(28)$ fm). For $H_2$, the energy level shift resulting from this correction is always less than 0.0001 cm$^{-1}$, whereas for $D_2$ it amounts to only 0.0002 cm$^{-1}$ or less. Nevertheless, in both cases, this correction has been included in our final results. According to our knowledge, there are no further corrections to the rovibrational energies which contribute above 0.001 cm$^{-1}$. The atomic hyperfine splittings are larger than that but are subtracted from the experimental dissociation energies. Recently reported[38] gerade−ungerade mixing and splitting effects in $H_2$ turned out to be smaller than $10^{-6}$ cm$^{-1}$ and thus are entirely negligible for the present purposes.

## 5. NUMERICAL APPROACH

A very accurate clamped nuclei potential for the $X^1\Sigma_g^+$ state was reported recently in ref 5. For the whole energy curve, an accuracy on the order of $10^{-9}$ cm$^{-1}$ has been reached. This is the most accurate potential to date for $H_2$ itself but also for any molecular system with two or more electrons. Increasing the accuracy to this level has been possible thanks to the discovery of analytic formulas for two-center two-electron integrals with exponential functions.[39] To achieve this high numerical accuracy, different basis sets were used, depending on the internuclear distance $R$. For $R<12$ bohr, the James−Coolidge basis functions[21] of the form

$$\psi_k(\vec{r}_1, \vec{r}_2) = (1 + \hat{P}_{12})(1 + \hat{i})$$
$$\exp(-\alpha(r_{1A} + r_{1B}) - \alpha(r_{2A} + r_{2B}))$$
$$\times r_{12}^{n_{1k}}(r_{1A} - r_{1B})^{n_{2k}}(r_{2A} - r_{2B})^{n_{3k}}(r_{1A} + r_{1B})^{n_{4k}}(r_{2A} + r_{2B})^{n_{5k}}$$

(16)

have been employed. The symmetry projector $(1 + \hat{P}_{12})$ ensures a singlet state, while the spatial projector $(1 + \hat{i})$ ensures the gerade symmetry. Since in the actual numerical calculations one can use only a finite number of basis functions, one has to somehow select the most appropriate finite subset of functions of eq 16. We assumed, therefore, that the finite basis consists of all functions $\psi_k$ with nonnegative integers $n_{ik}$ such that

$$\sum_{i=1}^{5} n_{ik} \leq \Omega$$

(17)

with $\Omega = 3-20$, and the final result is obtained by a numerical extrapolation with $\Omega \to \infty$. The nonlinear parameters were optimized separately for each internuclear distance $R$, and then the exponential convergence to a complete basis set as $\Omega \to \infty$ was observed.

To represent the electronic wave function at $12 \leq R \leq 20$ bohr, a special case of the Kolos and Wolniewicz basis[40] was used

$$\psi_k(\vec{r}_1, \vec{r}_2)$$
$$= (1 + \hat{P}_{12})(1 + \hat{i}) \exp(-(r_{1A} + r_{2B})) r_{12}^{n_{1k}} r_{1A}^{n_{2k}} r_{1B}^{n_{3k}} r_{2A}^{n_{4k}} r_{2B}^{n_{5k}}$$

(18)

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**Table 1. Theoretically Predicted Dissociation Energies (in cm$^{-1}$) of All 302 Bound States of H$_2$$^a$**

| $v$\$J$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|---|---|
| 0 | 36118.0696 | 35999.5827 | 35763.6964 | 35412.5507 | 34949.2721 | 34377.8800 | 33703.1726 | 32930.5991 |
| 1 | 31956.9034 | 31844.3290 | 31620.2311 | 31286.6781 | 30846.6902 | 30304.1479 | 29663.6809 | 28930.5440 |
| 2 | 28031.0670 | 27924.2753 | 27711.7087 | 27395.3676 | 26978.1720 | 26463.8724 | 25856.9411 | 25162.4519 |
| 3 | 24335.6787 | 24234.5818 | 24033.3726 | 23733.9878 | 23339.2543 | 22852.8015 | 22278.9563 | 21622.6265 |
| 4 | 20867.7039 | 20772.2598 | 20582.3263 | 20299.7818 | 19927.3669 | 19468.6008 | 18927.6785 | 18309.3586 |
| 5 | 17626.1400 | 17536.3593 | 17357.7260 | 17092.0653 | 16742.0411 | 16311.0741 | 15803.2433 | 15223.1787 |
| 6 | 14612.2901 | 14528.2461 | 14361.0627 | 14112.5194 | 13785.2138 | 13382.4836 | 12908.3120 | 12367.2247 |
| 7 | 11830.1543 | 11751.9964 | 11596.5661 | 11365.6062 | 11061.6626 | 10688.0095 | 10248.5600 | 9747.7694 |
| 8 | 9286.9790 | 9214.9526 | 9071.7726 | 8859.1575 | 8579.6206 | 8236.3999 | 7833.3746 | 7374.9763 |
| 9 | 6994.0292 | 6928.5057 | 6798.3271 | 6605.2057 | 6351.6504 | 6040.9022 | 5676.8602 | 5264.0027 |
| 10 | 4967.6786 | 4909.1996 | 4793.1191 | 4621.1702 | 4395.9005 | 4120.6166 | 3799.3225 | 3436.6592 |
| 11 | 3230.9712 | 3180.3202 | 3079.9265 | 2931.5894 | 2737.9677 | 2502.5403 | 2229.5680 | 1924.0695 |
| 12 | 1815.8955 | 1774.2213 | 1691.8517 | 1570.7364 | 1413.7847 | 1224.8610 | 1008.8062 | 771.5140 |
| 13 | 766.7551 | 735.8177 | 675.0810 | 586.8399 | 474.5979 | 343.1936 | 199.1012 | 51.2532 |
| 14 | 144.7964 | 127.6357 | 94.9453 | 50.2393 | 0.0265$^b$ | | | |

| $v$\$J$ | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 |
|---|---|---|---|---|---|---|---|---|
| 0 | 32066.1266 | 31116.1067 | 30087.1493 | 28986.0061 | 27819.4682 | 26594.2780 | 25317.0575 | 23994.2505 |
| 1 | 28110.4874 | 27209.6288 | 26234.3321 | 25191.0967 | 24086.4605 | 22926.9171 | 21718.8492 | 20468.4759 |
| 2 | 24385.9548 | 23533.3534 | 22610.7880 | 21624.5312 | 20580.8960 | 19486.1590 | 18346.4985 | 17167.9474 |
| 3 | 20889.1803 | 20084.3279 | 19214.0114 | 18284.3049 | 17301.3289 | 16271.1794 | 15199.8715 | 14093.2980 |
| 4 | 17618.8479 | 16861.6882 | 16043.6518 | 15170.6479 | 14248.6434 | 13283.5982 | 12281.4160 | 11247.9099 |
| 5 | 14575.9499 | 13866.9601 | 13101.8471 | 12286.3973 | 11426.4734 | 10527.9578 | 9596.7126 | 8638.5554 |
| 6 | 11764.1860 | 11104.4981 | 10393.7108 | 9637.5433 | 8841.8215 | 8012.4332 | 7155.3007 | 6276.3735 |
| 7 | 9190.5379 | 8582.1192 | 7928.0390 | 7234.0292 | 6505.9792 | 5749.9080 | 4971.9605 | 4178.4321 |
| 8 | 6866.1012 | 6312.0299 | 5718.3612 | 5090.9637 | 4435.9509 | 3759.6871 | 3068.8309 | 2370.4348 |
| 9 | 4807.3140 | 4312.2229 | 3784.5601 | 3230.5444 | 2656.8077 | 2070.4770 | 1479.3467 | 892.2132 |
| 10 | 3037.8559 | 2608.7032 | 2155.5628 | 1685.4344 | 1206.1180 | 726.5520 | 257.5346 | |
| 11 | 1591.8264 | 1239.4455 | 874.5218 | 506.0045 | 145.0445 | | | |
| 12 | 520.1248 | 263.4848 | 13.3741 | | | | | |

| $v$\$J$ | 16 | 17 | 18 | 19 | 20 | 21 | 22 | 23 |
|---|---|---|---|---|---|---|---|---|
| 0 | 22632.0799 | 21236.5171 | 19813.2627 | 18367.7376 | 16905.0813 | 15430.1579 | 13947.5677 | 12461.6638 |
| 1 | 19181.8142 | 17864.6524 | 16522.5351 | 15160.7573 | 13784.3676 | 12398.1776 | 11006.7791 | 9614.5672 |
| 2 | 15956.3587 | 14717.3851 | 13456.4677 | 12178.8362 | 10889.5174 | 9593.3530 | 8295.0256 | 6999.0945 |
| 3 | 12957.2014 | 11797.1591 | 10618.5796 | 9426.7112 | 8226.6608 | 7023.4255 | 5821.9382 | 4627.1316 |
| 4 | 10188.7828 | 9109.6212 | 8015.9040 | 6913.0252 | 5806.3338 | 4701.1940 | 3603.0755 | 2517.6864 |
| 5 | 7659.2518 | 6664.5260 | 5660.0900 | 4651.6971 | 3645.2264 | 2646.8145 | 1663.0640 | 701.3929 |
| 6 | 5381.6434 | 4477.1860 | 3569.2356 | 2664.3109 | 1769.4191 | 892.4054 | 42.5995 | |
| 7 | 3375.8309 | 2570.9911 | 1771.2705 | 984.8942 | 221.6033 | | | |
| 8 | 1672.1303 | 982.4662 | 311.5626 | | | | | |
| 9 | 319.5464 | | | | | | | |

| $v$\$J$ | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 |
|---|---|---|---|---|---|---|---|---|
| 0 | 10976.5735 | 9496.2237 | 8024.3709 | 6564.6364 | 5120.5483 | 3695.5928 | 2293.2796 | 917.2285 |
| 1 | 8225.7696 | 6844.4839 | 5474.7238 | 4120.4784 | 2785.7900 | 1474.8629 | 192.2238 | |
| 2 | 5710.0438 | 4432.3453 | 3170.5449 | 1929.3851 | 713.9904 | | | |
| 3 | 3444.0280 | 2277.8701 | 1134.3209 | 19.7931$^b$ | | | | |
| 4 | 1451.1807 | 410.5020 | | | | | | |

$^a$ $v$ and $J$ are the vibrational and rotational quantum numbers, respectively. Error estimation for individual states is given in the Supporting Information.
$^b$ This state is entirely due to nonadiabatic effects. Since it does not appear at the adiabatic approximation, its energy may be substantially less accurate than the energies of the remaining rovibrational states.

with $\Omega$ up to 16. This basis, which may be viewed as a generalized Heitler—London basis (it contains the Heitler—London function),

is needed to correctly describe molecular dissociation. At $R = 12$ bohr, the accuracy achieved with the basis set of eq 18 is close to

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## Table 2. Theoretically Predicted Dissociation Energies (in cm$^{-1}$) of All 598 Bound States of D$_2$[a]

| $v\backslash J$ | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 36748.3634 | 36688.5828 | 36569.2963 | 36391.0490 | 36154.6478 | 35861.1488 | 35511.8412 | 35108.2289 | 34652.0088 | 34145.0488 | 33589.3635 |
| 1 | 33754.7463 | 33697.0758 | 33582.0029 | 33410.0597 | 33182.0337 | 32898.9554 | 32562.0824 | 32172.8812 | 31733.0063 | 31244.2778 | 30708.6583 |
| 2 | 30880.2430 | 30824.6456 | 30713.7129 | 30547.9643 | 30328.1686 | 30055.3317 | 29730.6810 | 29355.6472 | 28931.8440 | 28461.0461 | 27945.1666 |
| 3 | 28122.7615 | 28069.2076 | 27962.3556 | 27802.7132 | 27591.0311 | 27328.2917 | 27015.6934 | 26654.6328 | 26246.6848 | 25793.5810 | 25297.1880 |
| 4 | 25480.6486 | 25429.1157 | 25326.3000 | 25172.6976 | 24969.0422 | 24716.2938 | 24415.6231 | 24068.3944 | 23676.1459 | 23240.5687 | 22763.4852 |
| 5 | 22952.7114 | 22903.1852 | 22804.3772 | 22656.7728 | 22461.0894 | 22218.2657 | 21929.4464 | 21595.9654 | 21219.3265 | 20801.1827 | 20343.3156 |
| 6 | 20538.2479 | 20490.7226 | 20395.9113 | 20254.2889 | 20066.5579 | 19833.6368 | 19556.6462 | 19236.8915 | 18875.8444 | 18475.1232 | 18036.4718 |
| 7 | 18237.0868 | 18191.5664 | 18100.7600 | 17965.1331 | 17785.3739 | 17562.3826 | 17297.2573 | 16991.2773 | 16645.8854 | 16262.6681 | 15843.3359 |
| 8 | 16049.6405 | 16006.1398 | 15919.3685 | 15789.7833 | 15618.0596 | 15405.0808 | 15151.9249 | 14859.8479 | 14530.2666 | 14164.7400 | 13764.9495 |
| 9 | 13976.9722 | 13935.5186 | 13852.8377 | 13729.3782 | 13565.8044 | 13362.9849 | 13121.9801 | 12844.0261 | 12530.5179 | 12182.9911 | 11803.1038 |
| 10 | 12020.8819 | 11981.5173 | 11903.0111 | 11785.8056 | 11630.5553 | 11438.1169 | 11209.5363 | 10946.0334 | 10648.9863 | 10319.9134 | 9960.4560 |
| 11 | 10184.0153 | 10146.7989 | 10072.5866 | 9961.8154 | 9815.1328 | 9633.3864 | 9417.6115 | 9169.0172 | 8888.9705 | 8578.9799 | 8240.6789 |
| 12 | 8470.0026 | 8435.0143 | 8365.2566 | 8261.1634 | 8123.3777 | 7952.7421 | 7750.2867 | 7517.2160 | 7254.8939 | 6964.8287 | 6648.6575 |
| 13 | 6883.6348 | 6850.9801 | 6785.8889 | 6688.7948 | 6560.3401 | 6401.3676 | 6212.9089 | 5996.1728 | 5752.5308 | 5483.5039 | 5190.7489 |
| 14 | 5431.0906 | 5400.9066 | 5340.7582 | 5251.0815 | 5132.5237 | 4985.9347 | 4812.3575 | 4613.0166 | 4389.3065 | 4142.7793 | 3875.1345 |
| 15 | 4120.2289 | 4092.6936 | 4037.8462 | 3956.1303 | 3848.2050 | 3714.9379 | 3557.3966 | 3376.8392 | 3174.7048 | 2952.6049 | 2712.3169 |
| 16 | 2960.9710 | 2936.3160 | 2887.2361 | 2814.1894 | 2717.8581 | 2599.1427 | 2459.1559 | 2299.2164 | 2120.8431 | 1925.7521 | 1715.8578 |
| 17 | 1965.8035 | 1944.3335 | 1901.6362 | 1838.1950 | 1754.7324 | 1652.2069 | 1531.8105 | 1394.9679 | 1243.3394 | 1078.8290 | 903.6027 |
| 18 | 1150.4486 | 1132.5743 | 1097.0897 | 1044.5231 | 975.6684 | 891.5869 | 793.6143 | 683.3726 | 562.7936 | 434.1618 | 300.1927 |
| 19 | 534.7343 | 521.0330 | 493.9347 | 454.0526 | 402.3180 | 339.9993 | 268.7360 | 190.6028 | 108.2387 | 25.1501 | |
| 20 | 143.4642 | 134.8278 | 117.9548 | 93.6691 | 63.2806 | 28.7401 | | | | | |
| 21 | 1.6642 | 0.0491[b] | | | | | | | | | |

| $v\backslash J$ | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 | 20 | 21 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 32987.0905 | 32340.4669 | 31651.8060 | 30923.4758 | 30157.8783 | 29357.4315 | 28524.5520 | 27661.6407 | 26771.0694 | 25855.1707 | 24916.2279 |
| 1 | 30128.2296 | 29505.1695 | 28841.7298 | 28140.2145 | 27402.9610 | 26632.3216 | 25830.6476 | 25000.2755 | 24143.5140 | 23262.6347 | 22359.8626 |
| 2 | 27386.2346 | 26786.3718 | 26147.7718 | 25472.6790 | 24763.3702 | 24022.1367 | 23251.2697 | 22453.0464 | 21629.7184 | 20783.5020 | 19916.5706 |
| 3 | 24759.4845 | 24182.5401 | 23568.4939 | 22919.5347 | 22237.8832 | 21525.7751 | 20785.4464 | 20019.1210 | 19228.9994 | 18417.2497 | 17586.0005 |
| 4 | 22246.8277 | 21692.6167 | 21102.9411 | 20479.9386 | 19825.7789 | 19142.6472 | 18432.7304 | 17698.2055 | 16941.2288 | 16163.9280 | 15368.3950 |
| 5 | 19847.6143 | 19316.0545 | 18750.6790 | 18153.5798 | 17526.8807 | 16872.7226 | 16193.2502 | 15490.6008 | 14766.8946 | 14024.2276 | 13264.6654 |
| 6 | 17561.7401 | 17052.8634 | 16511.8438 | 15940.7327 | 15341.6146 | 14716.5931 | 14067.7784 | 13397.2768 | 12707.1824 | 11999.5701 | 11276.4914 |
| 7 | 15389.7037 | 14903.6716 | 14387.2068 | 13842.3268 | 13271.0842 | 12675.5536 | 12057.8202 | 11419.9700 | 10764.0828 | 10092.2265 | 9406.4537 |
| 8 | 13332.6805 | 12869.8040 | 12378.2591 | 11860.0373 | 11317.1686 | 10751.7089 | 10165.7299 | 9561.3111 | 8940.5334 | 8305.4757 | 7658.2131 |
| 9 | 11392.6185 | 10953.3842 | 10487.3206 | 9996.4033 | 9482.6509 | 8948.1137 | 8394.8655 | 7824.9967 | 7240.6106 | 6643.8215 | 6036.7566 |
| 10 | 9572.3616 | 9157.4667 | 8717.6828 | 8254.9820 | 7771.3865 | 7268.9587 | 6749.7950 | 6216.0214 | 5669.7926 | 5113.2944 | 4548.7496 |
| 11 | 7875.8101 | 7486.2101 | 7073.7960 | 6640.5542 | 6188.5304 | 5719.8236 | 5236.5818 | 4741.0024 | 4235.3355 | 3721.8929 | 3203.0627 |
| 12 | 6308.1321 | 5945.1055 | 5561.5208 | 5159.4021 | 4740.8480 | 4308.0294 | 3863.1902 | 3408.6539 | 2946.8363 | 2480.2668 | 2011.6212 |
| 13 | 4876.0459 | 4541.2881 | 4188.4733 | 3819.6987 | 3437.1601 | 3043.1557 | 2640.0964 | 2230.5252 | 1817.1485 | 1402.8863 | 990.9510 |
| 14 | 3588.2093 | 3283.9721 | 2964.5198 | 2632.0792 | 2289.0159 | 1937.8510 | 1581.2918 | 1222.2810 | 864.0776 | 510.3933 | 165.6395 |
| 15 | 2455.7797 | 2185.0946 | 1902.5323 | 1610.5491 | 1311.8159 | 1009.2686 | 706.1933 | 406.3736 | 114.3694 | | |
| 16 | 1493.2790 | 1260.3555 | 1019.6781 | 774.1419 | 527.0394 | 282.2304 | 44.4834 | | | | |
| 17 | 720.1223 | 531.2062 | 340.1405 | 150.8950 | | | | | | | |
| 18 | 164.1866 | 30.3695 | | | | | | | | | |

| $v\backslash J$ | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 23956.4683 | 22978.0571 | 21983.0935 | 20973.6071 | 19951.5567 | 18918.8293 | 17877.2405 | 16828.5352 | 15774.3900 | 14716.4151 | 13656.1575 |
| 1 | 21437.3699 | 20497.2704 | 19541.6158 | 18572.3932 | 17591.5237 | 16600.8620 | 15602.1976 | 14597.2554 | 13587.6991 | 12575.1334 | 11561.1078 |
| 2 | 19031.0480 | 18129.0038 | 17212.4502 | 16283.3399 | 15343.5655 | 14394.9594 | 13439.2953 | 12478.2906 | 11513.6089 | 10546.8645 | 9579.6270 |
| 3 | 16737.3351 | 15873.2873 | 14995.8389 | 14106.9182 | 13208.4000 | 12302.1065 | 11389.8096 | 10473.2340 | 9554.0614 | 8633.9359 | 7714.4708 |
| 4 | 14556.6818 | 13730.7962 | 12892.7006 | 12044.3114 | 11187.4992 | 10324.0917 | 9455.8769 | 8584.6075 | 7712.0074 | 6839.7795 | 5969.6154 |
| 5 | 12490.2391 | 11702.9433 | 10904.7348 | 10097.5334 | 9283.2241 | 8463.6608 | 7640.6720 | 6816.0677 | 5991.6492 | 5169.2212 | 4350.6073 |
| 6 | 10539.9706 | 9792.0047 | 9034.5628 | 8269.5895 | 7499.0087 | 6724.7301 | 5948.6581 | 5172.7034 | 4398.7986 | 3628.9187 | 2865.1080 |
| 7 | 8708.8007 | 8001.2872 | 7285.9202 | 6564.6983 | 5839.6198 | 5112.6937 | 4385.9547 | 3661.4828 | 2941.4313 | 2228.0638 | 1523.8081 |
| 8 | 7000.8179 | 6335.3630 | 5663.9281 | 4988.6099 | 4311.5357 | 3634.8825 | 2960.9045 | 2291.9703 | 1630.6160 | 979.6255 | 342.1539 |

**Table 2. Continued**

| $v\backslash J$ | 22 | 23 | 24 | 25 | 26 | 27 | 28 | 29 | 30 | 31 | 32 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 9 | 5421.5600 | 4800.4013 | 4175.4879 | 3549.0832 | 2923.5329 | 2301.3016 | 1685.0260 | 1077.5947 | 482.2723 | | |
| 10 | 3978.4290 | 3404.6679 | 2829.8912 | 2256.6490 | 1687.6692 | 1125.9370 | 574.8194 | 38.2756 | | | |
| 11 | 2681.3328 | 2159.3251 | 1639.8473 | 1125.9722 | 621.1627 | 129.4853 | | | | | |
| 12 | 1543.7728 | 1079.8706 | 623.4674 | 178.7378 | | | | | | | |
| 13 | 584.9779 | 189.2547 | | | | | | | | | |

| $v\backslash J$ | 33 | 34 | 35 | 36 | 37 | 38 | 39 | 40 | 41 | 42 | 43 |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 0 | 12595.1047 | 11534.6886 | 10476.2901 | 9421.2440 | 8370.8452 | 7326.3541 | 6289.0044 | 5260.0106 | 4240.5776 | 3231.9113 | 2235.2318 |
| 1 | 10547.1215 | 9534.6279 | 8525.0406 | 7519.7400 | 6520.0811 | 5527.4021 | 4543.0351 | 3568.3189 | 2604.6139 | 1653.3230 | 715.9165 |
| 2 | 8613.4269 | 7649.7624 | 6690.1076 | 5735.9218 | 4788.6608 | 3849.7912 | 2920.8076 | 2003.2555 | 1098.7610 | | |
| 3 | 6797.2565 | 5883.8701 | 4975.8879 | 4074.9000 | 3182.5291 | 2300.4554 | 1430.4494 | 574.4182 | | | |
| 4 | 5103.2079 | 4242.2662 | 3388.5358 | 2543.8247 | 1710.0382 | 889.2289 | | | | | |
| 5 | 3537.6706 | 2732.3404 | 1936.6489 | 1152.7828 | 383.1585 | | | | | | |
| 6 | 2109.5182 | 1364.4607 | 632.4843 | | | | | | | | |
| 7 | 831.3351 | 153.6817 | | | | | | | | | |

[a] $v$ and $J$ are the vibrational and rotational quantum numbers, respectively. Error estimation for individual states is given in the Supporting Information. [b] This state does not exist in the Born—Oppenheimer approximation and its energy may be substantially less accurate than the energies of the remaining rovibrational states.

that obtained with the James—Coolidge basis. The Born—Oppenheimer energies obtained as described above were fitted with an analytic function of the form given in ref 27. We estimate that it represents the Born—Oppenheimer potential with accuracy better than $10^{-5}$ cm$^{-1}$. Fortran code to compute this analytic function can be supplied upon request.

For the evaluation of adiabatic, nonadiabatic, relativistic, and QED corrections, we have not used exponential functions, like Kolos and Wolniewicz in refs 40 and 22, because we have not yet developed integrals with inverse quadratic powers of electronic variables. Instead, we used explicitly correlated Gaussian (ECG) functions of the form

$$\psi_k(\vec{r}_1, \vec{r}_2)$$

$$= (1 + \hat{P}_{12})(1 \pm \hat{i}) \exp\left[-\sum_{i,j=1}^{2} A_{k,ij}(\vec{r}_i - \vec{s}_{k,i})(\vec{r}_j - \vec{s}_{k,j})\right]$$

$$(19)$$

where the symmetric $2 \times 2$ matrices $\mathbf{A}_k$ and vectors $\vec{s}_k$ (lying on the internuclear axis) contain nonlinear parameters, five per basis function, to be variationally optimized. The 1200-term ECG bases were optimized with respect to $\mathcal{E}_{el}$ for $R$ spread over the range 0—12 bohr and employed to evaluate all of the corrections. At larger values of $R$, the relativistic and QED corrections to the potential were represented using the asymptotic constants reported in refs 41 and 27. Details of numerical evaluations of adiabatic and nonadiabatic corrections were presented in refs 6 and 7, while the evaluation of relativistic and QED corrections to the potential was presented in ref 27.

It should be stressed that the method of computing the rovibrational levels employed in this work differs slightly from that of ref 27. In this reference, the relativistic and QED corrections were obtained directly by averaging the corrections to the potential with nuclear wave functions obtained in the adiabatic approximation. In the present work, the relativistic and QED corrections to the potential are used in the nonadiabatic equation for the nuclear motion, so we can deal with exceptional states which do not exist on the adiabatic level. The

corresponding corrections to the rovibrational levels were obtained as appropriate differences in calculated energies. Thus, the present "$\alpha^2$" energies contain very small contributions of the fourth and higher order in $\alpha$ as well as the first and higher order in $\alpha^2/\mu_n$. Similarly, the "$\alpha^3$" energies contain some very small contributions from the fifth and higher powers of $\alpha$. For low values of the vibrational quantum number $v$, both approaches give results differing by 0.0001 cm$^{-1}$ or less. At the highest values of $v$, apart from exceptional states described later on, the differences reach 0.0005 cm$^{-1}$, i.e., are of the order of the neglected recoil corrections. These differences appear only at the relativistic level. The QED corrections differ always less than 0.0001 cm$^{-1}$.

## 6. RESULTS FOR HYDROGEN AND DEUTERIUM MOLECULES

In Tables 1 and 2, we present the complete rovibrational spectrum of molecular hydrogen and deuterium in the electronic ground state $(X\ ^1\Sigma_g^+)$ in terms of dissociation energies with a precision of about 0.001 cm$^{-1}$ for $D_2$ and from 0.001 to 0.005 cm$^{-1}$ for $H_2$. The individual adiabatic, nonadiabatic, relativistic, and QED contributions for each level of $H_2$ and $D_2$ are listed in the Supporting Information files associated with this article (the very small finite-size contribution is included in the relativistic correction). The estimated theoretical uncertainties corresponding to each level are also listed in these files. The largest uncertainty comes from the $\alpha^4$ and higher-order QED corrections, which have been included only approximately, see eq 14, and from the higher-order $\mathcal{O}(\mu_n^{-5/2})$ NAPT corrections. Other significant sources of uncertainty are the neglected nonadiabatic relativistic effects. To estimate the uncertainty of each rovibrational level, we used the following procedure. We assumed that the error caused by the neglect of the relativistic recoil term can be estimated as $m_e/\mu_n$ times the $\alpha^2$ correction and, analogously, times the $\alpha^3$ correction to account for the missing QED recoil term. Similarly, we calculate the contribution to the error budget from the missing higher-order nonadiabatic terms as proportional to $m_e/\mu_n$ times the second-order
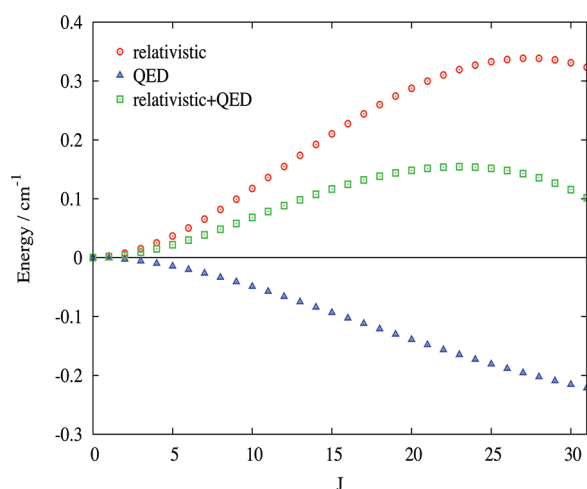
**Figure 1.** $J$ dependence of the relativistic and QED contributions to the rotational excitation energies at $v = 0$. The relativistic and QED corrections to the ground, $J = 0$ level are 0.5318(5) cm$^{-1}$ and 0.1964(8) cm$^{-1}$, respectively.
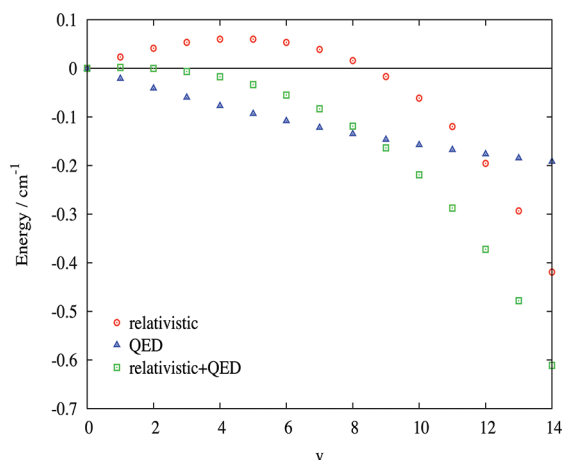


**Figure 2.** Vibrational quantum number dependence of the relativistic and QED contributions to the excitation energies at $J = 0$. The relativistic and QED corrections to the ground, $v = 0$ level are 0.5318(5) cm$^{-1}$ and 0.1964(8) cm$^{-1}$, respectively.

**Table 3. Dissociation Energies (in cm$^{-1}$) of H$_2$ and D$_2$ in Their Ground State—A Comparison with the Experiment**

| | $D_0$/cm$^{-1}$ | |
| --- | --- | --- |
| | H$_2$ | D$_2$ |
| experiment (1993) | 36118.06(4)[a] | 36748.32(7)[a] |
| experiment (2004) | 36118.062(10)[b] | 36748.343(10)[b] |
| experiment (2009/10) | 36118.06962(37)[c] | 36748.36286(68)[d] |
| theory | 36118.0696(11) | 36748.3634(9) |
| difference | 0.0000(12) | 0.0005(11) |

[a] Ref 66. [b] Ref 67. [c] Ref 1. [d] Ref 2.

**Table 4. The Lowest Rotational and Vibrational Excitation Energies (in cm$^{-1}$)**

| | H$_2$ | |
| --- | --- | --- |
| | $J = 0 \rightarrow 1$ | $v = 0 \rightarrow 1$ |
| theory | 118.486812(9) | 4161.1661(9) |
| experiment | 118.48684(10)[a] | 4161.1660(3)[b] |
| difference | −0.00003(10) | 0.0001(9) |

| | D$_2$ | |
| --- | --- | --- |
| | $J = 0 \rightarrow 1$ | $v = 0 \rightarrow 1$ |
| theory | 59.780615(3) | 2993.6171(2) |
| experiment | 59.78130(95)[c] | 2993.6130(19)[d] |
| difference | −0.00068(95) | 0.0041(19) |

[a] Ref 68. [b] Ref 46. [c] Ref 2. [d] Ref 45.

last observed" and "presumably bound". However, if we assign the up-to-date value of $D_0$ to the (0,0) level, the state observed by Dabrowski becomes a resonance located 0.05 cm$^{-1}$ above the dissociation threshold. This value is an order of magnitude smaller than the accuracy declared by Dabrowski; therefore, from the experimental point of view, the question whether this state is bound or not remains open. In the D$_2$ spectrum, we predict the existence of only one such level (21,1) with $D_0$ = 0.05 cm$^{-1}$. In this case, it is the adiabatic correction which makes this state bound. We note also the presence of another level located just below the dissociation threshold—the (21,0) state with $D_0 = 1.66$ cm$^{-1}$. This state, in contrast, is a regular one, accommodated already by the Born–Oppenheimer potential.

The $v$ and $J$ dependence of the relativistic and QED corrections to the rotational and vibrational excitation energies (relative the ground $v = 0, J = 0$ level) is shown in Figures 1 and 2. It may be pointed out that individual terms in eqs 11 and 12, like, e.g, mass velocity, Darwin, Breit or Araki-Sucher ones, lead to a monotonic dependence on $v$ or $J$. The nonmonotonic behavior observed in Figures 1 and 2 is due to cancellation effects and can be rationalized on the basis of the different $R$ dependence of the corresponding corrections to the potential. One may observe that the QED correction is not much smaller than the relativistic one and that the neglect of the former would lead to a qualitatively incorrect $v$ or $J$ dependence of the relativistic + QED contribution.

Theoretical predictions for the ground rovibrational state of H$_2$ and D$_2$ have already been presented by us in ref 27. Here, in Table 3, we compare these results with the most recent

nonadiabatic correction. Another part of the uncertainty comes from the incomplete treatment of the higher-order QED effects. As previously,[27] we conservatively estimate that the $\mathscr{E}^{(4)}$ terms other than the one-loop term of eq 14 as well as all higher-order $\mathscr{E}^{(n)}$ terms, $n > 4$, contribute at most 50% of the value of $\mathscr{E}^{(4)}_{\text{one-loop}}$. The quadratic sum of the four error components described above leads to the overall uncertainty on $D_0$ or any other computed energy difference.

Among the levels listed in Tables 1 and 2, we note a couple of curiosities—the bound levels, which are absent in the Born–Oppenheimer approximation. Such levels do not reveal themselves until the finite mass corrections are taken into account. In H$_2$, there are two such "nonadiabatic" levels: $(v,J) = (3,27)$ and (14,4), with dissociation energies of about 19.79 cm$^{-1}$ and 0.03 cm$^{-1}$, respectively. The former state was observed by Dabrowski[19] as lying 36098.04 cm$^{-1}$ above the (0,0) level, which corresponds to $D_0 = 20.03$ cm$^{-1}$. The latter one, located 36 118.12 cm$^{-1}$ above the reference state, she describes as "the

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dx.doi.org/10.1021/ct200438t | J. Chem. Theory Comput. XXXX, XXX, 000–000

**Table 5. Energy of Rotational Excitations $\Delta E(J)$ in $H_2$ ($v = 0$) with Respect to the Ground Level ($v = 0, J = 0$)—A Comparison with the Experimental Results of Salumbides et al.[27a]**

| $J$ | $\Delta E_{theo}(J)$ | $\Delta E_{exptl}(J)$ | $\delta(theo - exptl)$ | $\Delta E_{theo}^{QED}(J)$ | $\Delta E_{exptl}^{QED}(J)$ |
|---|---|---|---|---|---|
| 1 | 118.486812(9) | 118.48684(10) | −0.00003(10) | −0.001030(4) | −0.00100(10) |
| 2 | 354.37313(3) | 354.3733(2) | −0.0002(2) | −0.00307(1) | −0.0029(2) |
| 3 | 705.51883(5) | 705.5189(3) | −0.0001(3) | −0.00610(2) | −0.0060(3) |
| 4 | 1168.79743(9) | 1168.7982(2) | −0.0008(2) | −0.01005(4) | −0.0093(2) |
| 5 | 1740.1895(1) | 1740.1895(3) | −0.0000(3) | −0.01487(6) | −0.0148(3) |
| 6 | 2414.8970(2) | 2414.898(5) | −0.001(5) | −0.02050(8) | −0.019(5) |
| 7 | 3187.4705(2) | 3187.472(5) | −0.002(5) | −0.0268(1) | −0.025(5) |
| 8 | 4051.9430(3) | 4051.943(5) | −0.000(5) | −0.0338(1) | −0.034(5) |
| 9 | 5001.9628(4) | 5001.963(5) | −0.000(5) | −0.0414(2) | −0.041(5) |
| 10 | 6030.9202(5) | 6030.921(5) | −0.001(5) | −0.0494(2) | −0.049(5) |
| 11 | 7132.0634(6) | 7132.066(5) | −0.003(5) | −0.0578(2) | −0.055(5) |
| 12 | 8298.6014(6) | 8298.600(5) | 0.001(5) | −0.0665(3) | −0.068(5) |
| 13 | 9523.7916(7) | 9523.794(7) | −0.002(7) | −0.0754(3) | −0.073(7) |
| 14 | 10801.0121(9) | 10801.008(9) | 0.004(9) | −0.0846(3) | −0.089(9) |
| 15 | 12123.819(1) | 12123.83(1) | −0.01(1) | −0.0938(4) | −0.08(1) |
| 16 | 13485.990(1) | 13485.99(1) | −0.00(1) | −0.1030(4) | −0.10(1) |

[a] The two last columns show contributions to this energy from the QED effects: $\Delta E_{theo}^{QED}(J)$, predicted in our calculations, and $\Delta E_{exptl}^{QED}(J)$, extracted from the experimental data by subtracting our relativistic energies from the measured values given in column $\Delta E_{exptl}(J)$. All entries in $cm^{-1}$.
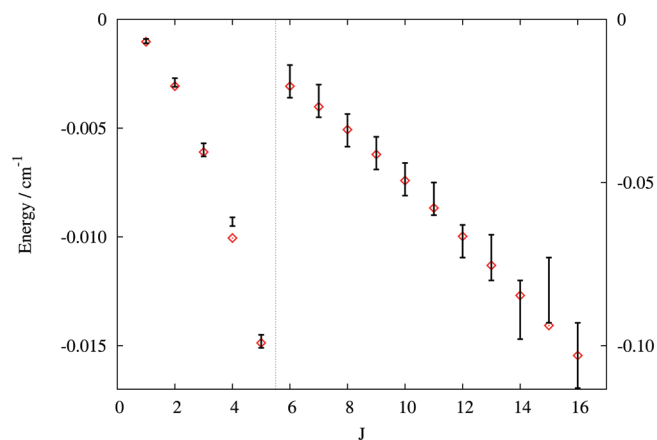


**Figure 3.** QED contributions to the rotational excitation energies at $v = 0$. Comparison of the present theoretical calculations (open diamonds) with the experimental data of ref 29. The left/right energy scale is for the levels to the left/right from the vertical line. The extent of the vertical bars shows the experimental uncertainties (listed in Table 5). The theoretical uncertainties (not shown) are at least an order of magnitude smaller than the experimental ones, except for $J = 4$ and $J = 5$, when they are 5 times smaller.

**Table 6. Vibrational Excitation Energies $E(v, J = 0) - E(v = 0, J = 0)$ for $H_2$ and Their Differences with the Experimental Values of Dabrowski[19] ($\delta_{exptl}$) and with the Best Previous Theoretical Values by Wolniewicz[26] ($\delta_{Wol}$)[a]**

| $v$ | theory | $\delta_{exptl}$ [b] | $\delta_{Wol}$ [c] |
|---|---|---|---|
| 1 | 4161.1661(9) | 0.03 | −0.001(1) |
| 2 | 8087.0026(17) | 0.07 | 0.000(2) |
| 3 | 11782.3908(25) | 0.03 | −0.001(3) |
| 4 | 15250.3656(32) | 0.06 | −0.002(3) |
| 5 | 18491.9296(37) | 0.01 | −0.002(4) |
| 6 | 21505.7795(43) | 0.00 | −0.004(4) |
| 7 | 24287.9152(47) | 0.01 | −0.004(5) |
| 8 | 26831.0906(50) | −0.07 | −0.003(5) |
| 9 | 29124.0404(52) | −0.05 | −0.004(5) |
| 10 | 31150.3909(51) | −0.08 | −0.004(5) |
| 11 | 32887.0983(49) | −0.03 | −0.004(5) |
| 12 | 34302.1740(42) | −0.03 | −0.004(4) |
| 13 | 35351.3145(31) | −0.05 | −0.003(3) |
| 14 | 35973.2731(16) | −0.11 | 0.000(2) |

[a] All energies in $cm^{-1}$. [b] Dabrowski[19] estimates the uncertainty of the measurements as 0.1 $cm^{-1}$. [c] Wolniewicz[26] does not give uncertainties for individual levels. He estimates overall accuracy as 0.001 $cm^{-1}$. The error estimation in this column comes only from the uncertainty of our calculations.

experimental data. Our present theoretical value of the dissociation energy of $H_2$, $D_0 = 36\,118.0696(11)$ $cm^{-1}$, differing very slightly from that of ref 27, agrees very well with the value $36\,118.06962(37)$ $cm^{-1}$ derived experimentally by Liu et al.[1] The dissociation energies for $D_2$ are $36\,748.3634(9)$ $cm^{-1}$ from theory and $36\,748.36286(68)$ $cm^{-1}$ from the most recent experiment.[2] The perfect agreement with the sophisticated high-resolution measurements (see also ref 42 for a confirmation of the result from ref 2) indicates that we control numerical accuracy of the included energy contributions as well as all physical effects down to 0.001 $cm^{-1}$. It is worth emphasizing that this excellent agreement would have been impossible

without including the Araki-Sucher term[43,44] and the interatomic distance dependence of the two-electron Bethe logarithm.

In Table 4, we compare our predictions for the lowest rotational and vibrational excitation energies. Agreement with the experimental values for $H_2$ is excellent, but for the vibrational excitation in $D_2$, a small discrepancy (of 2 experimental $\sigma$) is observed. Note that the experimental vibrational energies shown in this table are not measured directly but are extracted from a set of experimental literature lines fitted to the Dunham expansion.

**Table 7. Comparison of the Theoretical and Experimental Quadrupole Transition Energies in $H_2$. $\delta$ is their difference and carries the combined experimental/theoretical uncertainty. All energies in $cm^{-1}$.**

| | | $S_0(J)$ | | | |
|---|---|---|---|---|---|
| $J$ | theory | experiment[53] | $\delta$ | experiment[29] | $\delta$ |
| 0 | 354.373 13(3) | 354.373 50(40) | −0.000 37(40) | 354.373 3(2) | −0.000 2(2) |
| 1 | 587.032 02(4) | 587.032 11(17) | −0.000 09(17) | 587.032 1(3) | 0.000 0(3) |
| 2 | 814.424 30(6) | 814.424 73(8) | −0.000 43(10) | 814.424 9(2) | −0.000 6(2) |
| 3 | 1 034.670 68(8) | 1 034.670 24(3) | 0.000 44(9) | 1 034.670 6(3) | 0.000 1(3) |
| 4 | 1 246.099 54(9) | 1 246.098 11(17) | 0.001 43(19) | 1 246.100(5) | 0.000(5) |
| 5 | 1 447.280 93(11) | 1 447.278 82(41) | 0.002 11(42) | 1 447.282(5) | −0.002(5) |

| | $Q_1(J)$ | | | | $S_1(J)$ | | |
|---|---|---|---|---|---|---|---|
| $J$ | theory | experiment[54] | $\delta$ | | theory | experiment[54] | $\delta$ |
| 0 | | | | | 4497.8384(9) | 4497.8391(2) | −0.0007(9) |
| 1 | 4155.2538(9) | 4155.25469(8) | −0.0009(9) | | 4712.9046(9) | 4712.9054(2) | −0.0008(9) |
| 2 | 4143.4653(9) | 4143.4660(3) | −0.0007(9) | | 4917.0063(10) | 4917.0069(3) | −0.0006(10) |
| 3 | 4125.8726(9) | 4125.8739(4) | −0.0013(10) | | 5108.4029(10) | 5108.4040(6) | −0.0011(12) |
| 4 | 4102.5820(9) | 4102.582(4) | 0.000(4) | | | | |

| | $Q_2(J)$ | | | | $S_2(J)$ | | |
|---|---|---|---|---|---|---|---|
| $J$ | theory | experiment[54] | $\delta$ | | theory | experiment[54] | $\delta$ |
| 0 | | | | | 8406.3608(18) | 8406.365(2) | −0.004(3) |
| 1 | 8075.3074(17) | 8075.3114(6) | −0.0040(18) | | 8604.2152(18) | 8604.2189(8) | −0.0037(20) |
| 2 | 8051.9877(17) | 8051.991(7) | −0.003(7) | | 8785.5244(18) | 8785.529(6) | −0.005(6) |
| 3 | 8017.1831(17) | 8017.19(1) | −0.01(1) | | | | |

**Table 8. Comparison of the Theoretical and Experimental Quadrupole Transition Energies in $D_2$. $\delta$ is their difference and carries the combined experimental/theoretical uncertainty. All energies in $cm^{-1}$.**

| | | $S_0(J)$ | | | $S_1(J)$ | |
|---|---|---|---|---|---|---|
| $J$ | theory | experiment[55] | $\delta$ | theory | experiment[56] | $\delta$ |
| 0 | 179.06710(1) | 179.068(2) | −0.001(2) | 3166.3605(2) | 3166.3596(40) | 0.0009(40) |
| 1 | 297.53374(1) | 297.533(3) | 0.001(3) | 3278.5231(2) | 3278.5222(40) | 0.0009(40) |
| 2 | 414.64845(2) | 414.648(2) | 0.000(2) | 3387.2626(2) | 3387.2606(50) | 0.0020(50) |
| 3 | 529.90025(2) | 529.900(4) | 0.000(4) | 3492.0937(2) | 3492.0913(40) | 0.0024(40) |
| 4 | 642.80664(2) | 642.806(4) | 0.001(4) | | | |
| 5 | 752.91993(3) | 752.923(20) | −0.003(20) | | | |
| 6 | 859.83237(3) | 859.845(20) | −0.013(20) | | | |

| | | $O_1(J)$ | | | $Q_1(J)$ | |
|---|---|---|---|---|---|---|
| $J$ | theory | experiment[56] | $\delta$ | theory | experiment[56] | $\delta$ |
| 1 | | | | 2991.5070(2) | 2991.5043(40) | 0.0027(40) |
| 2 | 2814.5500(2) | 2814.5459(40) | 0.0041(40) | 2987.2934(2) | 2987.2955(40) | −0.0021(40) |
| 3 | 2693.9733(2) | 2693.9723(40) | 0.0010(40) | 2980.9894(2) | 2980.9882(40) | 0.0012(40) |
| 4 | 2572.645 0(2) | 2572.6428(50) | 0.0022(50) | 2972.6141(2) | 2972.6128(50) | 0.0013(50) |

The error estimation of the obtained value is one standard deviation of this fit.[45,46] We can also compare our result for $D_2$ with recent fully nonadiabatic relativistic calculations through order $\alpha^2$ (including all recoil terms of the order of $\alpha^2/\mu_n$) performed by Bubin et al.[45] For the energy difference of rotationless $v = 1$ and $v = 0$ states of $D_2$, these authors obtained 2993.6326(10) $cm^{-1}$, in perfect agreement with our value 2993.6326(2) $cm^{-1}$ obtained neglecting recoil terms. The authors of ref 45 attributed a discrepancy of their value with experimental results to the missing QED correction, unknown when their work was published. In fact, when our QED correction, amounting to −0.0155 $cm^{-1}$, is added, a small

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disagreement of 0.004(2) cm$^{-1}$, the same as shown in Table 4, remains.

A detailed comparison of the theoretical rotational excitation energies with a very recent experimental determination[29] is presented in Table 5. The error estimation assigned to the theoretical energy differences has been computed in the same fashion as the uncertainty for the individual levels, described earlier. In general, the assumed theoretical uncertainties are much smaller than the experimental ones. Very good agreement between the theoretical and experimental values is observed for all measured levels up to $J = 16$, except for $J = 4$, where a $4\sigma$ unexplained discrepancy is present.

In the two last columns of Table 5, we also present the pure QED contribution to each measured rotational level obtained by subtracting the nonrelativistic and our relativistic energies from either the total theoretical or the experimental values. The comparison of the theoretical and experimental QED contributions is shown in Figure 3. The observed agreement is remarkably good (except for $J = 4$), confirming the accuracy of both the measurement and the calculations. To our knowledge, this agreement represents the first observation of QED effects in a molecular spectrum. Specifically, these effects include the electron self-energy (interaction of the electron with the vacuum fluctuations of the electromagnetic field), the vacuum polarization (electron–positron virtual pair creation), and the retardation of the electron–electron interaction.[9] The conventional relativistic quantum mechanics based on the Dirac–Coulomb (DC) or Dirac–Coulomb–Breit (DCB) equations[31] neglects this complicated physics. Had we assumed the presence of exactly two electrons in the molecule and solved the DC or DCB equations using the direct perturbation theory (DPT) expansion in even powers of $\alpha$,[47,48] then all theoretical points in Figure 3 would have lain very close to the straight line $E = 0$. The deviation from this line is a quantitative demonstration of QED contribution to the rotational excitation energies of $H_2$. It may be pointed out in this context that due to the Brown–Ravenhall disease,[49] the eigenenergies of the DC or DCB equations are not precisely defined[50] and have an intrinsic uncertainty on the order of $\alpha^3$,[51] the same as the leading QED effects. Thus, when adding the $\alpha^3$ QED contribution to relativistic energies obtained using methods other than DPT, one should take special care to avoid double counting.

Whereas the effects of QED are well seen in the rotational spectrum, their influence on the bond length in $H_2$ is very small. The rotational constant $B$, defined as half of the smallest rotational spacing, decreases only by about $8 \times 10^{-6}$ in relative terms, which leads to an increase of the H–H bond distance (assumed to be proportional to $B^{-1/2}$) by merely $3 \times 10^{-6}$ Å. One should note, however, that for very weakly bound dimers, like e.g. $He_2$, the QED effects may significantly affect the bond length.[52]

It appears that the experimental pure vibrational excitation energies ($J = 0$) have not been measured with accuracy comparable to that of pure rotational ones ($v = 0$) of ref 29. In Table 6, we show a comparison of our values with the experimental data of Dabrowski[19] and with the theoretical values of Wolniewicz.[26] The agreement in both cases is very good, although it should be kept in mind that the accuracy of Dabrowski's results is limited. She estimates it as 0.1 cm$^{-1}$ without referring to any specific part of the spectrum. We observed, however, that for some high-lying levels (i.e., the highest bound levels shown in Table 4 of ref 19), her energies differ from ours by 0.2–0.4 cm$^{-1}$, i.e., much more

than our estimated uncertainties. The excellent agreement between ours and Wolniewicz's results, seen in Table 6, is likely due to the fact that the contribution of the two-electron QED effects, neglected by Wolniewicz, is small for the presented vibrational energy differences.

Some highly accurate values of the $Q$ and $S$ branch quadrupole transition frequencies of $H_2$ and $D_2$ are available in the literature[53–56] and are compared with our results in Tables 7 and 8. Both for $H_2$ and for $D_2$ we observe now some disagreements between theory and experimental results. The most significant discrepancies occur for the $S_0(2) - S_0(5)$ transitions in $H_2$ measured by Jennings and Brault.[53] Their transition energies differ from 5 up to 15 experimental $\sigma$ from our values. The reason for this discrepancy is not obvious to us. We speculate that an explanation may come from a possible underestimation of higher-order nonadiabatic effects, which are larger for $H_2$ than $D_2$. An alternative explanation, put forward for consideration by Campargue,[57] is a small pressure shift affecting the experimental result. On the other hand, we observe good agreement of our predictions with somewhat less accurate $S_0(J)$ transition energies that can be obtained from very recent measurement by Salumbides et al.[29] [except for the $S_0(2)$ line related to a similar exception noted in Table 5 for $J = 4$]. For the $Q_1$ and $S_1$ transitions, the discrepancies exceed the experimental error but fit within the sum of the theoretical and experimental uncertainties. Among the $Q_2$ and $S_2$ transitions, two lines ($J = 1$) do not conform to the above description and show discrepancies almost twice the size of the sum of these two uncertainties. Campargue,[57] on the basis of his own measurements and a comparison with Rahn and Rosasco's results,[58] suggests that the discrepancy in the $Q_1$ branch may be due to the calibration of the spectra of ref 54. What is more, we observe very good agreement of theoretical line positions with the measurements by Ferguson et al.[59] for higher transitions (not shown in Tables): $S_4(0)$, $S_4(1)$, and $S_5(1)$. The differences (and the experimental uncertainties) are 0.0008(36), 0.0001(10), and 0.0014(200) cm$^{-1}$, respectively.

For $D_2$ (see Table 8), we find general agreement with the measurements of Jennings et al.[55] and of McKellar and Oka.[56] The differences $\delta$ between the experimental and theoretical frequencies fit well within the experimental uncertainties of several thousandths of cm$^{-1}$. We observe, however, a discrepancy with recently reported measurements[60] of $S_1(0)$ and $S_1(1)$ lines. The experimental values 3166.3620(2) cm$^{-1}$ and 3278.5220(2) cm$^{-1}$ differ from our predictions by several combined experimental/theoretical uncertainties.

## 7. CONCLUSION

The accuracy of about 0.001 cm$^{-1}$ for most of the dissociation energies of rovibrational levels of $H_2$ and isotopomers has been achieved due to the recent progress made in two directions. The first one enabled a complete treatment of the leading $\alpha^3$ QED effects. In particular, an effective approach to calculating the many-electron Bethe logarithm and mean values of singular operators, like the Araki-Sucher term,[43,44] has been developed and is given in refs 27, 61 and 62. The second direction, indispensable to reaching this accuracy, is the nonadiabatic perturbation theory, NAPT,[6,7,63] which enables a rigorous approach to the finite nuclear mass effects beyond the adiabatic approximation. However, nonadiabatic contributions to the relativistic and QED energies (the so-called recoil corrections)

still remain to be evaluated. These corrections as well as the higher-order nonadiabatic $\mathcal{O}(\mu_n^{-5/2})$, the complete $\alpha^4$ QED, and the leading term in $\alpha^5$ correction have to be evaluated in order to reach a $10^{-6}$ cm$^{-1}$ level of accuracy, where the H$_2$ spectrum becomes sensitive to uncertainties in the electron–proton mass ratio and in the proton charge radius.[64] One may speculate that at this level of precision exotic forces between hadrons carried by very weakly interacting sub-electronvolt particles (WISPs) might also become spectro-scopically observable.[65]

## ■ ASSOCIATED CONTENT

**Ⓢ Supporting Information.** Components of the dissociation energy as well as its uncertainty for all the rovibrational levels of H$_2$ and D$_2$. This material is available free of charge via the Internet at http://pubs.acs.org/.

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## ■ ACKNOWLEDGMENT

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