

# Variational calculations of excited states with zero total angular momentum (vibrational spectrum) of H<sub>2</sub> without use of the Born–Oppenheimer approximation

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Very accurate, rigorous and fully variational, all-particle, non-Born–Oppenheimer calculations of the vibrational spectrum of the H<sub>2</sub> molecule have been performed. Very high accuracy has been achieved by expanding the wave functions in terms of explicitly correlated Gaussian functions with preexponential powers of the internuclear distance. An indicator of the high accuracy of the calculations is the new upper bound for the H<sub>2</sub> nonrelativistic nonadiabatic ground state energy equal to  $-1.164\,025\,030\,0$  hartree. © 2003 American Institute of Physics.

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We recently introduced a new correlated Gaussian basis set suitable for high accuracy nonadiabatic calculations on diatomic molecules<sup>1</sup> and showed that the basis is capable of providing the most accurate ground-state nonadiabatic energies of H<sub>2</sub> (Ref. 2) and LiH.<sup>3</sup> In this article we continue the validation of our approach by presenting highly accurate, variational, non-Born–Oppenheimer (non-BO) nonrelativistic calculations of the “vibrational spectrum” of the H<sub>2</sub> molecule. Although we use the term “vibrational spectrum,” the states we have calculated can be better characterized as states with the zero total angular momentum that is the sum of the angular momenta of the electrons and the nuclei. We calculate these states by using totally spherically symmetric wave functions dependent on the coordinates of both nuclei and electrons in an internal coordinate system that excludes the three coordinates describing the motion of the center of mass of the molecule. By describing our method as “variational” we mean that the energies of the ground and excited states in our calculations are obtained by direct diagonalization of the Hamiltonian matrix.

Such direct calculations of the whole vibrational spectrum have not previously been reported in the literature. So far the only direct nonadiabatic calculation of H<sub>2</sub> vibrational levels has been the early work of Wolniewicz,<sup>4</sup> which only considered the ground and the first excited state.

A by-product of the calculations is a new variational upper-bound for the ground state energy of the H<sub>2</sub> molecule. This new upper-bound, as well as the variational upper-bounds to the excited vibrational energies, should provide a very accurate reference for future nonadiabatic molecular calculations and for evaluating the quality of methodologies where the nonadiabatic effects are determined as “correc-

tions” to the BO approximation. The present high-accuracy results may also be used in the future to estimate the relativistic effects in the vibrational spectrum of H<sub>2</sub> as a difference of the transition energies and the experimental energies.

In the nonadiabatic molecular approach that does not invoke the BO approximation regarding the separability of the electronic and nuclear motions, all particles (nuclei and electrons) are treated equally. Without invoking any approximations, the total nonrelativistic Hamiltonian can be separated into an operator representing the translational motion of the center of mass and an operator representing the internal energy. For H<sub>2</sub> we perform this separation by making transformation to an internal reference frame with the origin at one of the two nuclei,

$$\mathbf{r} = \begin{bmatrix} \mathbf{r}_1 \\ \mathbf{r}_2 \\ \mathbf{r}_3 \end{bmatrix} = \begin{bmatrix} \mathbf{R}_2 - \mathbf{R}_1 \\ \mathbf{R}_3 - \mathbf{R}_1 \\ \mathbf{R}_4 - \mathbf{R}_1 \end{bmatrix}, \quad (1)$$

where the  $\mathbf{R}_i$  are the original Cartesian coordinates in the laboratory coordinate system. This transformation to the internal coordinates together with the conjugate momentum transformation yields the nonadiabatic Hamiltonian for the internal energy of H<sub>2</sub> expressed in terms of coordinates of three pseudoparticles as

$$H = -\frac{1}{2} \left( \sum_{i=1}^3 \frac{1}{\mu_i} \nabla_i^2 + \sum_{i \neq j}^3 \frac{1}{M_1} \nabla_i' \nabla_j' \right) + \sum_{i=1}^3 \frac{q_0 q_i}{r_i} + \sum_{i < j}^3 \frac{q_i q_j}{r_{ij}}, \quad (2)$$

where  $\mu_i = M_1 M_i / (M_1 + M_i)$  is the reduced mass associated with the first and  $i$ th particles, and  $M_1$  is the mass of particle 1 (the reference nucleus). The potential energy is the same as

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in the total Hamiltonian but is now written using internal distance coordinates. The charges are mapped from the original particles as  $\{Q_1, Q_2, Q_3, Q_4\} \mapsto \{q_0, q_1, q_2, q_3\}$ . In the internal coordinates, the interparticle distances are:  $r_{ij} = |\mathbf{r}_i - \mathbf{r}_j| = |\mathbf{R}_{i+1} - \mathbf{R}_{j+1}|$  with  $r_j = |\mathbf{r}_j| = |\mathbf{R}_{j+1} - \mathbf{R}_1|$ . More information on the nonadiabatic Hamiltonian and eliminating the coordinates of the center of mass motion can be found in Ref. 1.

Explicitly correlated spherical Gaussians multiplied by powers of the internuclear distance were used as basis functions in the present calculations. As we showed before,<sup>1,2</sup> the preexponential powers of the internuclear distance allow us to describe the nuclei correlation effects. They are also important in generating nodes in the wave functions of the vibrational excited states. The general form of the basis function is (the prime represents vector/matrix transposition and  $\otimes$  is the Kronecker product symbol)

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(\mathbf{L}_k \mathbf{L}_k' \otimes \mathbf{I}_3) \mathbf{r}], \quad (3)$$

where for  $\text{H}_2$   $\mathbf{r}$  is a  $9 \times 1$  vector of the internal Cartesian coordinates of the three pseudoparticles,  $\mathbf{L}_k$  is  $3 \times 3$  rank 3 lower triangular matrix of nonlinear variation parameters, and  $\mathbf{I}_3$  is the  $3 \times 3$  identity matrix. To ensure the proper permutational symmetry of the two identical nuclei and the two electrons, the appropriate symmetry projections were applied to the basis functions. More details regarding the form of the symmetry projection operators can be found in Refs. 1 and 2. Using only spherical Gaussians we can only describe states with the zero total angular momentum. In order to consider rotationally excited states we would need to include in the basis functions angular factors. Such factors have been considered in recent works by Suzuki and Varga (see Ref. 7).

Our calculations were performed for the proton–electron mass ratio of 1836.152 667 5 taken from the CODATA 98.<sup>5</sup> We used the atomic units except where otherwise noted. Thus,  $\hbar = 1$ ,  $m_e = 1$ , energies are in hartrees, and distances are in bohrs.

The wave functions for the ground state and the excited states were obtained using the variational method by minimizing the energy of each state obtained through diagonalization in a separate calculation. The minimization was done with respect to the linear expansion coefficients,  $c_k$ , and with respect to the nonlinear parameters of the basis functions, i.e., the basis set exponent matrices,  $\mathbf{L}_k$ , and the powers of the internuclear distance,  $m_k$ .

In our previous non-BO calculations of the ground states of  $\text{H}_2$  and  $\text{LiH}^{2,3}$  we employed a procedure where we directly optimized the Rayleigh quotient with respect to both the linear and the nonlinear parameters,

$$E(\mathbf{L}, \mathbf{m}, \mathbf{c}) = \min_{\{\mathbf{L}, \mathbf{m}, \mathbf{c}\}} \frac{\mathbf{c}' \mathbf{H}(\mathbf{L}, \mathbf{m}) \mathbf{c}}{\mathbf{c}' \mathbf{S}(\mathbf{L}, \mathbf{m}) \mathbf{c}},$$

where  $\mathbf{H}(\mathbf{L}, \mathbf{m})$  and  $\mathbf{S}(\mathbf{L}, \mathbf{m})$  are the Hamiltonian and overlap matrices, respectively. Both are functions of the nonlinear parameters of the basis functions. In the optimization we used the analytically calculated gradients of the energy with respect to the linear and exponential nonlinear parameters.<sup>1</sup> The powers,  $m_k$ , were optimized separately.

In the present calculations we used a mixed approach. First we optimized a wave function for each state in the basis of 128 functions (175 functions for the highest, fourteenth, excited state) using the procedure based on analytical gradients to obtain a good first approximation. Then we continued the optimization using the stochastic variational method.<sup>6,7</sup> In this step we enlarged the basis set for each state by including additional basis functions with randomly selected nonlinear parameters and powers of the internuclear distance, and by subsequently optimizing these parameters of the functions in one-dimensional optimizations. After each addition of 100–200 new functions to the basis we carried out a cyclic one-dimensional optimization of each nonlinear parameter of every function in the basis set. Although the approach, unlike the approach based on the analytical gradient, does not usually provide a very well optimized set of parameters, it allows one to compensate for this by significantly increasing the basis set size. In the present calculations we used 3000 basis functions for each of the 15 calculated states. As will be shown next, with 3000 basis functions we noticeably lowered our previous variational upper-bound of the ground state energy of  $\text{H}_2$ .<sup>2</sup> This indicated to us that the stochastic variational approach is very effective in the energy minimization.

The non-BO wave functions of different excited states have to differ from each other by the number of “nodes” in terms of the internuclear distance,  $r_1$ . To accurately describe the node structures in all 15 states considered in the present calculations, a wide range of powers,  $m_k$ , had to be used. While in the previous calculations of the  $\text{H}_2$  ground state<sup>2</sup> the power range was 0–40, in the present calculations it was extended to 0–250. Also, as was the case in the previous calculations, we only used even powers.

All optimizations performed in this work have been carried out using the double precision (64 bit). A peril of significantly increasing number of terms in the expansions of the wave functions in such calculations is the numerical instability. To verify this point, all results presented in this work were recalculated with the quadruple precision (128 bit). No numerical inaccuracies have been detected.

The high degree of parallelism of the algorithm that underlies the stochastic variational method allowed development of a parallel implementation of the procedure. The calculations described here have been carried out using MPI (message passing interface) on several multiprocessor computer platforms. They included our “Beowulf” 16-processor SUN ULTRA 10 cluster, an IBM SP3 computer, and SGI ORIGIN 2000 super-computer. The calculations have been carried out continuously for over four months.

Table I contains total variational energies of the lowest 15 states corresponding to the rotational ground state ( $J = 0$ ) calculated with 3000 basis functions each. We also show the expectation values of the internuclear distance and its square calculated as average values using the optimized wave function of each state ( $\langle r_1 \rangle, \langle r_1^2 \rangle$ ). The energy for the ground state of  $-1.164\,025\,030\,0$  hartree is noticeably lower than our previously reported upper-bound<sup>2</sup> of  $-1.164\,025\,023\,2$  hartree. We are certain that for at least a few lowest excited states the quality of the results is very similar as for the ground state. However, for the highest

TABLE I. Nonadiabatic variational energies for 15 states of the H<sub>2</sub> molecule with zero total angular momentum (the ground rotational states) obtained with 3000 basis functions for each state and expectation values of the internuclear distance and the square of the internuclear distance,  $\langle r_1 \rangle$ ,  $\langle r_1^2 \rangle$ . Also, the nonrelativistic energies of Wolniewicz are presented for comparison. All quantities in atomic units.

$v$	$E$	$\langle r_1 \rangle$	$\langle r_1^2 \rangle$	$E$ (from Ref. 11)
0	-1.164 025 030 0	1.448 738 0	2.127 045 9	-1.164 025 018 5
1	-1.145 065 367 6	1.545 349 5	2.473 996 7	-1.145 065 362 9
2	-1.127 177 915 2	1.646 057 9	2.856 817 2	-1.127 177 932 4
3	-1.110 340 442 9	1.751 708 2	3.281 414 3	-1.110 340 485 5
4	-1.094 539 118 7	1.863 424 5	3.755 699 5	-1.094 539 194 0
5	-1.079 769 321 7	1.982 733 2	4.290 541 7	-1.079 769 480 3
6	-1.066 037 073 7	2.111 758 7	4.901 320 7	-1.066 037 284 9
7	-1.053 360 489 0	2.253 534 9	5.610 516 3	-1.053 360 825 8
8	-1.041 772 695 0	2.412 595 2	6.452 556 7	-1.041 773 113 9
9	-1.031 324 945 4	2.595 894 0	7.482 387 6	-1.031 325 470 8
10	-1.022 091 784 9	2.814 949 0	8.794 679 6	-1.022 092 487 6
11	-1.014 178 260 1	3.090 179 8	10.566 922	-1.014 179 153 6
12	-1.007 730 195 1	3.462 701 0	13.181 814	-1.007 731 197 9
13	-1.002 949 375 8	4.034 237 3	17.680 148	-1.002 950 463 3
14	-1.000 115 048 2	5.211 018 1	28.919 890	-1.000 115 976 2
<sup>a</sup>	-0.999 455 679 4			

<sup>a</sup>Nonrelativistic threshold.

states, where the number of nodes in the wave function is much higher, the quality of the calculations decreases, but we believe that it still allows determination of the transition energies, discussed next, with the accuracy similar to the experimental uncertainty, if not higher.

In Table I we also compare our total variational energies with the energies obtained by Wolniewicz. In his calculations Wolniewicz employed an approach where in the zeroth order the adiabatic approximation for the wave function was used (i.e., the wave function is a product of the ground state electronic wave function and a vibrational wave function) and he calculated the nonadiabatic effects as corrections.<sup>8,9</sup> In general the agreement between our results and the results of Wolniewicz is very good. However, one notices that the agreement is much better for the lower energies than for the higher ones. While for the two lowest states our energies are lower than those obtained by Wolniewicz, the energies for the higher states are progressively higher.

We found it interesting how the distribution of powers of  $r_1$  in the basis set changes with the increased excitation level. We demonstrate this change in Fig. 1 by showing the power distributions optimized for the  $v=0$ ,  $v=1$ , and  $v=14$  states. As expected, only one maximum in the power distribution appeared for the ground-state wave function, where there are no nodes and the wave function peaks near the ground-state equilibrium distance ( $\langle r_1 \rangle = 1.449$  bohr). For the first excited state, the distribution was somewhat wider, which seems to be a result of two overlapping peaks and reflects the presence of a maximum and a minimum in the wave function of this state. For the  $v=14$  state, whose wave function has 14 “nodes,” the power distribution became almost uniform in the 0–250 range.

Included in Table II is the comparison of the transition frequencies calculated from the energies obtained in this work with the experimental transition frequencies of Dabrowski.<sup>10</sup> To convert theoretical frequencies into wave numbers we used the factor of 1 hartree

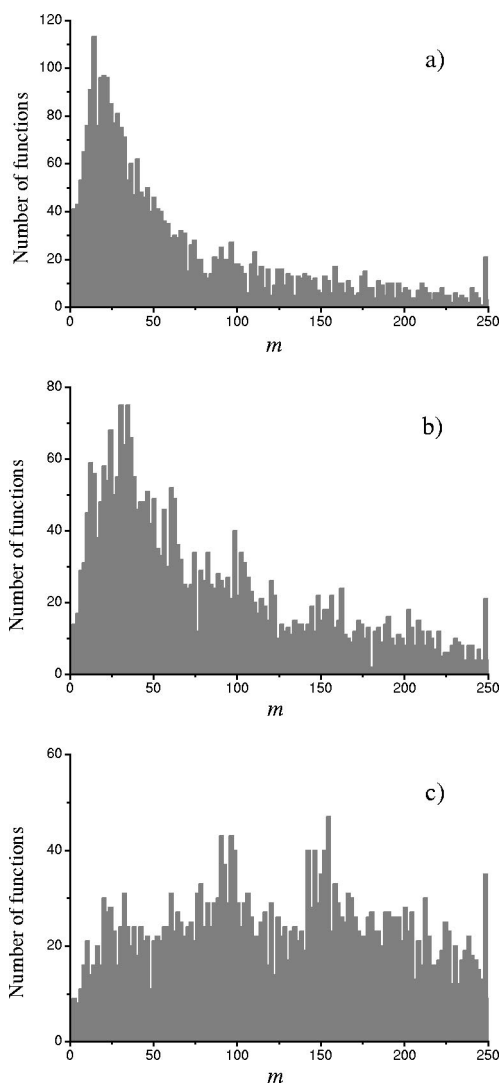


FIG. 1. The distribution of  $r_1$  powers for the states with  $v=0$  (a),  $v=1$  (b), and  $v=14$  (c).

TABLE II. Comparison of vibrational frequencies  $E_{v+1} - E_v$  (in  $\text{cm}^{-1}$ ) of  $\text{H}_2$  calculated from our non-Born–Oppenheimer energies with the experimental values of Dabrowski and with the results of Wolniewicz obtained using the conventional approach based on the potential energy curve. Differences between the calculated and the experimental results are shown in parentheses.

$v$	Experiment <sup>a</sup>	This work (Diff.)	Wolniewicz <sup>b</sup> (Diff.)	Wolniewicz <sup>c</sup> (Diff.)
0	4161.14	4161.165 (+0.025)	4161.163 (+0.023)	4161.167 (+0.027)
1	3925.79	3925.842 (+0.052)	3925.837 (+0.047)	3925.836 (+0.046)
2	3695.43	3695.398 (−0.032)	3695.392 (−0.038)	3695.389 (−0.041)
3	3467.95	3467.990 (+0.040)	3467.983 (+0.033)	3467.976 (+0.026)
4	3241.61	3241.596 (−0.014)	3241.577 (−0.033)	3241.564 (−0.046)
5	3013.86	3013.880 (+0.020)	3013.869 (+0.009)	3013.851 (−0.009)
6	2782.13	2782.189 (+0.059)	2782.161 (+0.031)	2782.136 (+0.006)
7	2543.25	2543.227 (−0.023)	2543.209 (−0.041)	2543.175 (−0.075)
8	2292.93	2293.016 (+0.086)	2292.993 (+0.063)	2292.950 (+0.020)
9	2026.38	2026.445 (+0.064)	2026.406 (+0.026)	2026.351 (−0.029)
10	1736.66	1736.818 (+0.158)	1736.776 (+0.116)	1736.707 (+0.047)
11	1415.07	1415.187 (+0.117)	1415.163 (+0.093)	1415.076 (+0.006)
12	1049.16	1049.269 (+0.109)	1049.250 (+0.090)	1049.139 (−0.021)
13	622.02	622.063 (+0.043)	622.098 (+0.078)	621.956 (−0.064)

<sup>a</sup>Reference 10.

<sup>b</sup>Reference 11 (nonrelativistic values).

<sup>c</sup>From Ref. 8 (includes relativistic and radiative corrections).

$= 219\,474.63137 \text{ cm}^{-1}$  from CODATA 98.<sup>5</sup> For all the frequencies our results are either within or very close to the experimental error bracket of  $0.1 \text{ cm}^{-1}$ . We hope that the present calculations will inspire a remeasurement of the vibrational spectrum of  $\text{H}_2$  with the accuracy lower than  $0.1 \text{ cm}^{-1}$ . With such high-precision results it would be possible to verify whether the larger differences between the calculated and the experimental frequencies for higher excitation levels, that now appear, are due to the relativistic and radiative effects.

Finally, in Table II we also compare our results for the transition energies with the results obtained by Wolniewicz in Refs. 8 and 9. Wolniewicz also calculated transition energies corrected for the relativistic effects and these results are also shown in Table II. Upon comparing the results one notices that our transition energies are, in general, very similar to Wolniewicz's nonrelativistic results. Both sets of results show higher positive discrepancies in comparison with the experimental values for the higher excitation levels. These discrepancies decrease somewhat when the relativistic ef-

fects are included. However, the insufficient accuracy of the experiment, as well as perhaps that of some of the theoretical results, does not allow one to carry out a more detailed analysis of the remaining discrepancies.

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