



## Non-adiabatic corrections to the energies of the pure vibrational states of H<sub>2</sub>

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### ABSTRACT

Nonrelativistic energies of all fifteen pure vibrational states of the H<sub>2</sub> molecule have been recalculated with much higher accuracy than before. In the calculations we employed explicitly correlated Gaussian functions and an approach where the Born–Oppenheimer (BO) approximation is not assumed. The wave function of each state was expanded in terms of 10000 Gaussians whose nonlinear parameters were optimized using a procedure involving the analytical energy gradient. The obtained non-BO energies combined with the recent BO adiabatic energies of Pachucki and Komasa [K. Pachucki, J. Komasa, J. Chem. Phys. 129 (2008) 034102] allowed us to determine new improved values of the non-adiabatic corrections for the considered states.

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### 1. Introduction

The Born–Oppenheimer approximation is central to the quantum mechanical calculations on molecular systems. For the majority of chemical problems the separation of the nuclear motion from the electronic motion that one makes in solving the Schrödinger equation within this approximation has an insignificant effect on the results. However, measurements involving high resolution gas-phase molecular spectroscopy, time-resolved laser spectroscopy, and other high-precision methods have been providing results that are impossible to match with theoretical calculations unless effects involving the coupling of the motions of the electrons and the nuclei in the studied system are accounted for. In the framework of the quantum mechanical molecular calculations these effects can be either described using the perturbation theory [1–3] or they can be incorporated in the model from the very beginning without starting from a simpler model that in the lowest order does not include the coupling. In the review summarizing their works on the H<sub>2</sub> molecules [4] Kolos and Wolniewicz expressed a view that in very accurate calculations on small molecular systems one should drop the idea of separating the electronic and nuclear motions from the very beginning and solve the complete Schrödinger equation describing all the particles involved in the system. Over the last four decades several works have appeared concerning calculations of energies and wave functions of molecular systems without assuming the BO approximation [1,5–10]. Our contribution to the field has been the development

of a non-BO approach that employs explicitly correlated Gaussian functions to calculate ground and excited states of atomic and molecular systems [11,12]. Unlike other approaches, our method is not limited to one- and two-electron diatomic systems. Examples of non-BO calculations, where we have considered molecules with more than two electrons, include the work of the vibrational transitions of the LiH molecule [13], the calculations of the ionization energy of BeH [14], the calculations of the ground state of H<sub>3</sub> [15], and the work on the electron affinities of the LiH and LiD molecules [16].

Even with explicitly correlated Gaussians rigorous non-BO variational calculations are currently limited to small molecular systems with a few electrons. For larger systems non-BO effects can be determined using the perturbation theory approach. Such an approach, for example, was used in the calculations of the H<sub>2</sub> molecule by Kolos and Wolniewicz [4] and very recently by Pachucki and Komasa [2,3]. In order to test the effectiveness of the perturbation calculations of the non-adiabatic effects very accurate non-BO energies are needed, which, when subtracted from the adiabatic energies, give the complete non-adiabatic energy corrections. These corrections can be directly compared with the corrections obtained using the perturbation theory. The most popular simple molecular system that have been used for testing the procedures for determining mass corrections to various molecular properties is the H<sub>2</sub> molecule. A year ago we published the results of the non-BO calculations of all fifteen bound pure vibrational states of this system using 5800 explicitly correlated Gaussians per state [17]. The calculations included the lowest order relativistic effects. The exponential parameters of the Gaussians were extensively optimized with a procedure that involved the gradient of the energy determined with respect to the Gaussian exponents. Since

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that publication a new 15.8 TFLOPS SGI Altix ICE system with 1392 processors was installed at the University of Arizona Computer Center. This provided us with an opportunity to revisit the H<sub>2</sub> calculations and, by extending the basis set for each of the fifteen bound vibrational states to 10000 basis functions, recalculate their non-BO energies with much higher accuracy. The results of the calculations, that lasted for more than a year, are presented in this work. Most of the computer time was used to optimize the wave functions and, as the Gaussian parameters for each state were optimized separately, the calculations for all states have been run simultaneously using either eight or sixteen processors per calculation. The results of this work include new values for the non-adiabatic corrections obtained using our new non-BO energies and the adiabatic energies taken from the work of Pachucki and Komasa [2].

Some of the reasons we deem important to carry out improved nonrelativistic non-BO calculations of the vibrational spectrum of H<sub>2</sub> are: (i) in our previous calculations [17], while the energies of the lower lying states were well converged, this was not the case for the upper half of the energy spectrum. In the calculations presented here the convergence has been significantly improved. We estimate that the maximum error of the new energies is now lower than  $1.4 \times 10^{-8}$  hartree. One needs to achieve this level of accuracy in order to determine the vibrational transitions with a comparable precision as offered by the currently available state-of-the-art experimental spectroscopy measurements; (ii) the H<sub>2</sub> molecule serves as a model for testing the accuracy of various methods used to perform quantum mechanical calculations on small molecular systems. Very accurate calculations of the H<sub>2</sub> spectrum can help to determine how to improve those new methods and whether the accuracy they offer is sufficient to adequately describe larger molecular systems; (iii) as the method we used in the present H<sub>2</sub> calculations does not assume the BO approximation, the non-adiabatic energy corrections can be determined directly without resorting to the perturbation theory (PT). As in all applications of the perturbation theory, there is always a question about the convergence of the PT series and whether it is adequately fast to provide good results at lower orders for the studied problem. The energies converged as tight as ours can provide a useful set of data for testing the PT convergence.

We start this work with a brief description of the method we used (a more complete description of the method can be found in our recent reviews [11,12]). The results and a discussion are presented in the last section.

## 2. The approach

The calculations presented here have been performed using the standard variational method applied separately to each state. The variational minimization has been applied to the total internal energy expressed as the expectation value of the internal nonrelativistic Hamiltonian,  $\hat{H}_{\text{nonrel}}$ , obtained from the ‘laboratory frame’ Hamiltonian by separating out the center-of-mass motion. For H<sub>2</sub> the internal Hamiltonian expressed in terms of the internal Cartesian coordinates with the center at one of the protons has the following form:

$$\hat{H}_{\text{nonrel}} = -\frac{1}{2} \left( \sum_{i=1}^3 \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{i=1}^3 \sum_{j \neq i}^3 \frac{1}{m_0} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^3 \frac{q_0 q_i}{r_i} + \sum_{i < j}^3 \frac{q_i q_j}{r_{ij}}. \quad (1)$$

In (1)  $q_0 = q_1 = 1$  are the charges of the protons and  $q_2 = q_3 = -1$  are the electron charges,  $\mathbf{r}_i$ ,  $i = 1, 2, 3$ , are the position vectors of the second proton and the two electrons with respect to the proton placed in the center of the internal coordinate system,  $r_i$  are their

lengths,  $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$ ,  $m_0 = m_1 = 1836.15267261 m_e$  are the masses of the protons,  $m_2 = m_3 = 1$  are the electron masses [18], and  $\mu_i = m_0 m_i / (m_0 + m_i)$  is the reduced mass of particle  $i$ . It is important to note that the internal Hamiltonian (1) is spatially ‘isotropic’ (rotationally invariant). More information on the center-of-mass separation and the form of the internal Hamiltonian (1) can be found elsewhere [11,12].

As in the previous works the spatial part of the H<sub>2</sub> non-BO wave functions of the pure (rotation-less) vibrational states are expanded in terms of one-center, spherically symmetric explicitly correlated Gaussian functions multiplied by even powers ( $m_k$ ) of the distance between the protons,  $r_1$  [17,19–22]:

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (2)$$

where  $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3\}'$ ,  $\prime$  denotes the vector (matrix) transposition,  $A_k$  is a  $3 \times 3$  symmetric matrix of the Gaussian exponential parameters,  $I_3$  is a  $3 \times 3$  unit matrix, and  $\otimes$  denotes the Kronecker product. As one notices, the functions (2) are fully spherically symmetric and have the necessary radial flexibility (through the  $r_1^{m_k}$  factors) to describe radial nodes of the spherically symmetric wave functions representing rotation-less vibrational bound states of the internal Hamiltonian (1) considered in this work.

The variational minimization of the energy involved optimization of the linear coefficients of the expansion of the wave function in terms of the Gaussian basis functions, the Gaussian exponential parameters,  $A_k$ , and the pre-exponential  $r_1$  powers,  $m_k$  of the Gaussians (2). As  $\phi_k$  basis functions have to be square integrable one needs to impose restrictions on the elements of each  $A_k$  matrix to make it positive definite. In our approach this is accomplished by using the Cholesky-factored form of  $A_k$ ,  $A_k \equiv L_k L_k'$ , where  $L_k$  is a lower triangular matrix (all elements above the diagonal are zero). With the Cholesky-factored representation of  $A_k$ , this matrix is automatically positive definite for any real values of the  $L_k$  matrix elements. Thus the  $L_k$  matrix elements become optimization variables in our calculations. As mentioned, another set of variables that we optimize are the pre-exponential powers,  $m_k$ . Their values ranged from 0 to 250 in the present calculations. The pre-exponential  $r_1$  power of each Gaussian function was only optimized when the function was first added to the basis set. The permutation symmetry of the wave function was implemented by placing the symmetrization operator,  $(1 + P_{pp})(1 + P_{ee})$  ( $P_{pp}$  permutes the labels of protons and  $P_{ee}$  permutes the electron labels), in front of each basis function.

The key feature that differentiates our approach from other approaches utilizing explicitly correlated Gaussian functions is the use of the analytical energy gradient calculated with respect to the Gaussian exponential parameters in the variational energy minimization. Employing the gradient significantly accelerates the optimization process and allows achieving high accuracy in the calculation.

The present calculations concern all fifteen pure vibrational states ( $v = 0, 1, 2, \dots, 14$ ) of H<sub>2</sub>. The maximum number of basis functions used for each state was 10000. This is almost twice the number of functions used in our previous H<sub>2</sub> calculations [17]. More details about the procedure of growing the Gaussian basis set for H<sub>2</sub> can be found in our previous work [17]. The procedure consisted of adding groups of twenty functions and reoptimizing the whole set after each addition. In the reoptimization cycle the exponential parameters of each function were reoptimized once. After a 10000 function basis was generated for each state additional fifty reoptimization cycles were performed to further lower the energy.

The non-BO energies obtained in the calculations were used to calculate the non-adiabatic corrections. These corrections were obtained by subtracting the adiabatic vibrational energies recently published by Pachucki and Komasa [2] from our non-BO energies.

Non-BO calculations produce wave functions that depend on the internal coordinates of the nuclei and electrons. The wave functions for the ground and excited rotation-less states of H<sub>2</sub> considered in this work differ from each other in the number of the  $r_1$  radial nodes ( $r_1$  is the distance between the two protons). To describe this node structure we use plots of the nucleus–nucleus (proton–proton for H<sub>2</sub>) correlation functions defined as [23]:

$$g_i(\xi) = \langle \Psi_i(\mathbf{r}) | \delta(\mathbf{r}_1 - \xi) | \Psi_i(\mathbf{r}) \rangle = \int_{-\infty}^{\infty} |\Psi_i(\xi, \mathbf{r}_2, \mathbf{r}_3)|^2 d\mathbf{r}_2 d\mathbf{r}_3, \quad (3)$$

where  $\delta(\mathbf{r}_1 - \xi)$  is the 3-dimensional Dirac delta function and  $\Psi_i(\mathbf{r})$  is the wave function of the  $i$  state. The nucleus–nucleus correlation function (3) provides information on the structure of the molecular system in different states. In the results section we show plots of the correlation functions for some selected H<sub>2</sub> vibrational states.

### 3. The results

In Table 1, we present the total nonrelativistic energies for all fifteen pure vibrational states obtained in the calculations. The results obtained with 6000, 7000, 8000, 9000, and 10000 functions are presented to show the energy convergence pattern. There are two entries for 10000 functions for each state. The first corresponds to the energy obtained by enlarging the basis from 9000 to 10000 functions using the same procedure as used for the 6000 → 7000, 7000 → 8000, and 8000 → 9000 enlargements. The second 10000-function entry is the energy obtained by performing additional fifty optimization cycles of the 10000-function basis set. The increase of the basis from 5800 Gaussians used in our previous work [17] to the current 10000 Gaussians resulted in a noticeable lowering of the energies of all fifteen states. The improvement was not uniform (see the values in the parenthesis in Table 1). The largest energy lowering occurred for the top states (by  $\approx 10^{-8}$  hartree) and the smallest for the bottom states (by  $\approx 10^{-10}$  hartree).

As one can see the energy convergence becomes slightly worse for the higher states than for the lower ones. While for the lower states, the additional fifty optimization cycles have almost no effect on the energy, for the higher states some improvement was obtained. Overall the results show that our final non-BO energy for the highest vibrational state ( $\nu = 14$ ) is converged to about  $5 \times 10^{-9}$  hartree. For lower states the convergence is significantly better.

An important issue that needs to be addressed is the accuracy of our results. To estimate it we have performed an analysis of the convergence of our non-BO energies for all states using a nonlinear

**Table 2**

Non-adiabatic energy contributions,  $E^{\text{nonadiab}}$ , to the energies of the pure vibrational states of H<sub>2</sub>. The contributions are compared with the results of Wolniewicz [1] and with the results of Pachucki and Komasa [2,3]. The differences between our results presented in the second column and the results of Wolniewicz and of Pachucki and Komasa are given in the parenthesis. All values are in cm<sup>-1</sup>.

$\nu$	$E^{\text{nonadiab}}$	$E^{\text{nonadiab a}}$	$E^{\text{nonadiab b}}$	$E^{\text{nonadiab c}}$
0	-0.4991	-0.4988 (+0.0003)	-0.511 (-0.012)	-0.4990 (+0.0001)
1	-1.3357	-1.3350 (+0.0007)	-1.347 (-0.011)	-1.3355 (+0.0002)
2	-2.0922	-2.0913 (+0.0009)	-2.104 (-0.012)	-2.0922 (0.0000)
3	-2.7737	-2.7728 (+0.0009)	-2.785 (-0.011)	-2.7739 (-0.0002)
4	-3.3834	-3.3824 (+0.0010)	-3.395 (-0.012)	-3.3838 (-0.0004)
5	-3.9221	-3.9208 (+0.0013)	-3.934 (-0.012)	-3.9227 (-0.0006)
6	-4.3861	-4.3847 (+0.0014)	-4.398 (-0.012)	-4.3869 (-0.0008)
7	-4.7664	-4.7654 (+0.0020)	-4.779 (-0.013)	-4.7680 (-0.0016)
8	-5.0470	-5.0459 (+0.0011)	-5.059 (-0.012)	-5.0489 (-0.0019)
9	-5.1989	-5.1980 (+0.0009)	-5.210 (-0.011)	-5.2015 (-0.0026)
10	-5.1777	-5.1772 (+0.0005)	-5.187 (-0.009)	-5.1811 (-0.0034)
11	-4.9179	-4.9176 (+0.0003)	-4.926 (-0.008)	-4.9217 (-0.0038)
12	-4.3270	-4.3270 (+0.0000)	-4.333 (-0.006)	-4.3308 (-0.0038)
13	-3.2842	-3.2844 (-0.0002)	-3.287 (-0.003)	-3.2872 (-0.0030)
14	-1.6477	-1.6482 (-0.0005)	-1.646 (0.002)	-1.6498 (-0.0021)

<sup>a</sup> The results of Wolniewicz [1] taken from the paper of Pachucki and Komasa [2].

<sup>b</sup> The results of Pachucki and Komasa [2].

<sup>c</sup> The results of Pachucki and Komasa [3].

extrapolation procedure. The procedure is based on the following formula:  $E(K) = E(\infty) + \frac{A}{K^b}$ , that relates the energy obtained with  $K$  basis functions to the energy extrapolated to an infinite number of basis functions,  $E(\infty)$ , and to two constants,  $A$  and  $b$ .  $E(\infty)$ ,  $A$ , and  $b$  are determined using a least-squares fitting procedure using the energies obtained in the calculations for different values of  $K$ . The results of the extrapolation are shown in the last column of Table 1. They were calculated as differences between the energy values obtained with 10000 functions and the corresponding values estimated for the infinite number of basis functions. As one can see, the convergence is quite satisfactory particularly for the lowest states.

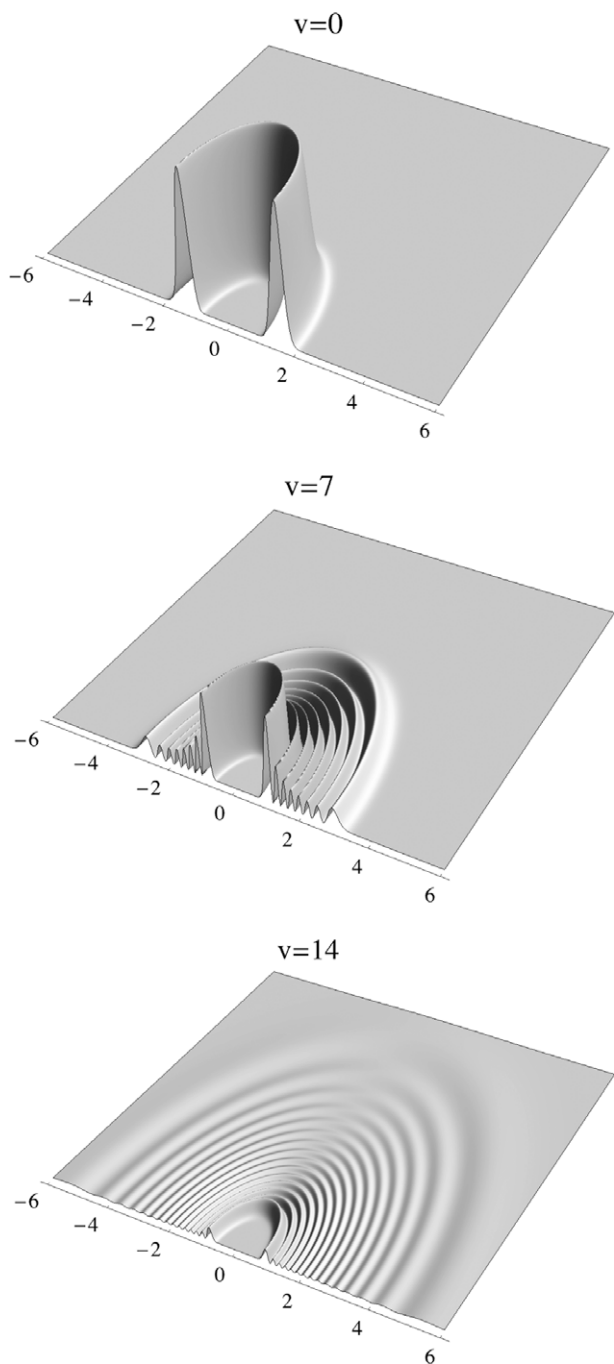
In Table 2, we show the values of the non-adiabatic energy calculated for each state by subtracting the adiabatic energies of Pachucki and Komasa [2] from our non-BO energies. As one can see these corrections increase from  $\nu = 0$  to  $\nu = 10$  and then decrease from  $\nu = 11$  to  $\nu = 14$ . Table 2 also includes a comparison of the adiabatic corrections obtained in the present calculations with the corrections obtained by Wolniewicz [1] and by Pachucki and Komasa [2,3]. In general, our results agree very well with the results of Wolniewicz. The largest difference is only 0.0020 cm<sup>-1</sup>.

**Table 1**

Convergence of the total non-BO energy with the number of basis functions,  $M$ . Energies are in hartrees. In the parenthesis by the nonrelativistic energy obtained with 10000 basis functions we show the energy lowering achieved by enlarging the basis set from 5800 to 10000 functions. The error in the energy shown in the last column was estimated as a difference between the value of the energy obtained from an extrapolation to an infinite number of basis functions and the energy obtained with 10000 basis functions.

$\nu$	$M = 7000$	$M = 8000$	$M = 9000$	$M = 10000$	$M = 10000^a$	Est. error
0	-1.16402503072	-1.16402503079	-1.16402503082	-1.16402503084	-1.16402503084	$(-2.1 \times 10^{-10})$ $6 \times 10^{-11}$
1	-1.14506537180	-1.14506537193	-1.14506537202	-1.14506537209	-1.14506537210	$(-5.6 \times 10^{-10})$ $5 \times 10^{-10}$
2	-1.12717793514	-1.12717793540	-1.12717793558	-1.12717793572	-1.12717793573	$(-1.3 \times 10^{-9})$ $9 \times 10^{-10}$
3	-1.11034047802	-1.11034047842	-1.11034047872	-1.11034047893	-1.11034047896	$(-1.7 \times 10^{-9})$ $9 \times 10^{-10}$
4	-1.09453917164	-1.09453917213	-1.09453917248	-1.09453917277	-1.09453917280	$(-2.2 \times 10^{-9})$ $1 \times 10^{-9}$
5	-1.07976944479	-1.07976944555	-1.07976944606	-1.07976944642	-1.07976944647	$(-3.5 \times 10^{-9})$ $2 \times 10^{-9}$
6	-1.06603723345	-1.06603723427	-1.06603723496	-1.06603723543	-1.06603723550	$(-3.9 \times 10^{-9})$ $2 \times 10^{-9}$
7	-1.05336075872	-1.05336075984	-1.05336076064	-1.05336076124	-1.05336076136	$(-5.2 \times 10^{-9})$ $3 \times 10^{-9}$
8	-1.04177303330	-1.04177303480	-1.04177303576	-1.04177303648	-1.04177303663	$(-6.7 \times 10^{-9})$ $3 \times 10^{-9}$
9	-1.03132537776	-1.03132537950	-1.03132538074	-1.03132538164	-1.03132538188	$(-8.6 \times 10^{-9})$ $4 \times 10^{-9}$
10	-1.02209238958	-1.02209239171	-1.02209239319	-1.02209239417	-1.02209239440	$(-1.0 \times 10^{-8})$ $4 \times 10^{-9}$
11	-1.01417905483	-1.01417905732	-1.01417905898	-1.01417906013	-1.01417906044	$(-1.2 \times 10^{-8})$ $4 \times 10^{-9}$
12	-1.00773110799	-1.00773111095	-1.00773111280	-1.00773111411	-1.00773111446	$(-1.4 \times 10^{-8})$ $5 \times 10^{-9}$
13	-1.00295039306	-1.00295039616	-1.00295039813	-1.00295039947	-1.00295039985	$(-1.4 \times 10^{-8})$ $5 \times 10^{-9}$
14	-1.00011594097	-1.00011594357	-1.00011594522	-1.00011594635	-1.00011594657	$(-1.2 \times 10^{-8})$ $5 \times 10^{-9}$

<sup>a</sup> The energy obtained after additional fifty optimization cycles.



**Fig. 1.** Proton–proton correlation functions,  $g_i(\xi)$ , for the  $v = 0, 7$ , and  $14$  pure vibrational states of the  $H_2$  molecule. The densities are shown as two-dimensional functions of the  $\xi_x$  and  $\xi_y$  coordinates with the  $\xi_z$  coordinate set to zero.

The Wolniewicz's results are slightly higher than ours except for the highest two states. Such a small difference can only come to play if the  $H_2$  calculations are performed at very high accuracy with including higher order relativistic and quantum electrodynamics (QED) effects.

The non-adiabatic energies obtained in the first of two recent works by Pachucki and Komasa [2] show larger differences with our results (the largest difference being  $-0.013 \text{ cm}^{-1}$ ). As it is stated in the Pachucki and Komasa paper, there is some inaccuracy in their results due to neglecting higher order non-adiabatic effects. This inaccuracy explains the differences with our results. Pachucki

and Komasa included these effects in the second of the two papers [3] and their results noticeably improved as can be seen from the comparison shown in Table 2. However, for the top seven states, while our results perfectly agree with the results of Wolniewicz, the results of Pachucki and Komasa show some larger deviations.

Finally, as an illustration of the results of the present calculations, we show in Fig. 1 plots of the proton–proton correlation functions for the rotation-less states of  $H_2$  are spherically symmetric, spherically symmetric are also the corresponding correlation functions. As such they could have been plotted on one-dimensional graphs, but we have chosen a two-dimensional representation to emphasize the 'atom' like character of the wave functions obtained for  $H_2$  (or any other system) with an approach that does not assume the Born–Oppenheimer approximation. The concentric rings in the correlation functions correspond to the radial vibrational maxima. With the increasing excitation level the molecule becomes increasingly more diffuse in space.

In a large-scale calculations such as these it is usually in order to comment on the computational resources used. As mentioned, the calculations have been performed on a distributed-memory computer cluster. The optimizations of the Gaussian exponential parameters of the basis sets used to expand the wave functions were by far the most time consuming steps of the calculations. The memory use was limited to only 1-2GB of RAM allocated on each processor and a very small scratch allocation.

#### 4. Summary

The main contribution of this work is the recalculation of the energies of all rotation-less vibrational states of the  $H_2$  molecule with much higher accuracy than done before. The new results enabled us to more accurately recalculate the non-adiabatic energy corrections for these states. The values of these corrections provide new standards for testing methods for calculating the non-adiabatic corrections using the perturbation theory. For example, they show that the procedure developed by Wolniewicz [1] nearly twenty years ago performs still somewhat better than the procedure recently presented by Pachucki and Komasa [3].

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