

Accurate non-Born-Oppenheimer calculations of the complete pure vibrational spectrum of D_2 with including relativistic corrections

Sergiy Bubin,¹ Monika Stanke,² and Ludwik Adamowicz^{3,4,a)}

¹*Department of Physics and Astronomy, Vanderbilt University, Nashville, Tennessee 37235, USA*

²*Department of Physics, Nicholas Copernicus University, ul. Grudziądzka 5, Toruń, PL 87-100, Poland*

³*Department of Chemistry and Biochemistry, University of Arizona, Tucson, Arizona 85721, USA*

⁴*Department of Physics, University of Arizona, Tucson, Arizona 85721, USA*

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In this work we report very accurate variational calculations of the complete pure vibrational spectrum of the D_2 molecule performed within the framework where the Born-Oppenheimer (BO) approximation is not assumed. After the elimination of the center-of-mass motion, D_2 becomes a three-particle problem in this framework. As the considered states correspond to the zero total angular momentum, their wave functions are expanded in terms of all-particle, one-center, spherically symmetric explicitly correlated Gaussian functions multiplied by even non-negative powers of the internuclear distance. The nonrelativistic energies of the states obtained in the non-BO calculations are corrected for the relativistic effects of the order of α^2 (where $\alpha = 1/c$ is the fine structure constant) calculated as expectation values of the operators representing these effects. © 2011 American Institute of Physics. [doi:10.1063/1.3625955]

I. INTRODUCTION

Quantum electrodynamics¹⁻³ provides a general theoretical framework for calculating energies of stationary bound states of atoms and molecules with a very high accuracy. In this framework an effective perturbation approach has been developed to account for relativistic effects in small systems. The zero-order level in this approach is the nonrelativistic Schrödinger equation. In this theory the relativistic corrections are proportional to different powers of the fine structure constant α (in atomic units $\alpha = 1/c$ where c is the speed of light). In this work the zero-order approximation is the nonrelativistic Schrödinger equation with the Hamiltonian representing the internal motion of the electrons and nuclei in the system obtained without assuming the Born-Oppenheimer (BO) approximation. In the calculation of the relativistic corrections we only consider terms proportional to α^2 .

Treating the nuclei and electrons on equal footing and not assuming the clamped nucleus approximation makes the problem of calculating stationary, bound states of a molecular system much more complicated than the problem of determining bound states of electrons in the field of stationary nuclei. The main complication comes from the need to describe not one type of the correlation effects, i.e., the electron-electron correlation, but three types, the electron-electron, nucleus-nucleus, and nucleus-electron correlations. This places additional demands on the basis functions which are used in expansions of the wave functions representing those stationary states. Also, as the purpose of a non-BO calculation is to describe the system with very high accuracy, the basis functions have to be capable of providing very accurate representations of the wave function.

We use the so-called explicitly correlated Gaussian functions (ECGF) in this work. It has been shown that exponential dependence on the inter-particle distances of these functions is very effective in describing the inter-electron correlation effects. The functions are also adequate for describing the nucleus-electron correlation effects. However, the strong nuclear-nuclear correlation is more difficult to describe, because it requires that the wave function practically vanishes when two nuclei approach each other very closely. This behavior, which happens to much lesser extent for electrons, can be described by inclusion of powers of the internuclear distances as pre-exponential multipliers in the ECGFs.⁴⁻⁶ For diatomic systems the multipliers include powers of only one distance – the internuclear separation. These type of functions have been shown to very effectively represent zero-angular-momentum bound states of small diatomics.^{7,8} In this work they are used for expanding the wave functions for all bound rotationless states of the D_2 molecule. These states are also called pure vibrational states, as their wave functions differ by the number of nodes they have in terms of the internuclear distance. The ground state has no nodes. However, as the level of excitation increases, states, whose wave functions have some small contributions from functions with nodes in terms of the electron-nucleus and electron-electron coordinates, may also appear. This effect is called state mixing in the approach based on the BO approximation. As in our approach no restrictions (other than the permutational symmetry restrictions) are placed on the wave function, the state mixing is automatically permitted to occur in the calculation. With that, very high accuracy solutions of the nonrelativistic problem can be obtained.

In recent years we have reported several non-BO calculations on small molecules including D_2 .⁹ The D_2 calculations were done with only 512 ECGFs. Recently we also calculated the lowest two D_2 pure vibrational states using much

^{a)} Author to whom correspondence should be addressed. Electronic mail: ludwik@u.arizona.edu.

more extended basis sets of 10 000 ECGFs.¹⁰ In this work 10 000 ECGFs are used to calculate all 22 pure vibrational states of the D₂ molecule.

The non-BO calculations presented in this work have been performed using the non-relativistic Hamiltonian obtained by rigorously separating out the motion of the center of mass from the laboratory-frame Hamiltonian. The “internal” Hamiltonian obtained this way is rotationally invariant and its eigenfunctions transform according to the irreducible representations of the group of 3D rotations (SO(3)). In particular, the ground state or any rotationless $J = 0$ state of a system with positive (natural) parity is represented by a spherically symmetric s -type wave function, which can be expanded in terms of spherically symmetric ECGFs. All zero-angular-momentum bound states (i.e., the pure vibrational states) of D₂ are such states.

As mentioned, the leading relativistic corrections of the order of α^2 are calculated in this work for the considered states. The algorithms for calculating these corrections using the non-BO wave functions expanded in terms of ECGFs were presented in our previous works.^{11–13}

There have been some very accurate calculations performed on D₂ by others. Wolniewicz calculated vibrational energies of D₂ using the conventional approach where the BO potential energy curve (PEC) of H₂ was calculated first, and, after adding to each PEC point the adiabatic, nonadiabatic, relativistic, and radiative corrections, it was used to calculate the vibrational energy levels.¹⁴ A similar approach was also recently applied by Piszczatowski *et al.*¹⁵ to calculate the dissociation energy of D₂ with very high accuracy. This was achieved by including not only α^2 relativistic corrections but also the quantum electrodynamics corrections of the order α^3 and α^4 (only the one-loop term).

In Sec. II, we briefly describe the method used in the calculations (a more complete description of the method can be found in our recent reviews^{4,5}). The results obtained in the calculations are presented and discussed in the last section.

II. THE METHOD USED IN THE CALCULATIONS

In this work we consider all existing 22 bound rotationless states of the D₂ molecule. Each state has been calculated independently. The conventional Rayleigh-Ritz variational method has been employed to minimize the energy and to optimize the wave function for each state. The energy is determined using the internal nonrelativistic Hamiltonian, \hat{H}_{nonrel} , obtained by explicitly and rigorously separating out the center-of-mass motion from the laboratory-frame Hamiltonian. The internal Hamiltonian for D₂ 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 Eq. (1), $q_0 = q_1 = 1$ are the charges of the nuclei and $q_2 = q_3 = -1$ are the electron charges, \mathbf{r}_i , $i = 1, 2, 3$, are the

position vectors of the second nucleus and the two electrons with respect to the first nucleus (placed in the center of the internal coordinate system; we call this nucleus the “reference particle”), r_i are their lengths, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, $m_0 = m_1 = 3670.4829654 m_e$ are the deuteron masses, $m_2 = m_3 = m_e = 1$ are the electron masses,¹⁶ and $\mu_i = m_0 m_i / (m_0 + m_i)$ is the reduced mass of particle i . One can describe Hamiltonian (1) as representing three “pseudoparticles” with charges equal to the charges of the original particles, but with masses changed to the reduce masses, moving in the central potential of the charge of the reference particle. The motions of the three pseudoparticles are coupled through the Coulomb interactions and through the so-called mass-polarization terms.

The Breit-Pauli Hamiltonian and the first-order perturbation theory have been used to calculate the relativistic corrections of the order of α^2 . This approach has been employed by others in very accurate calculations of light atoms and molecules before.^{17–19} The Breit-Pauli relativistic operators representing the mass-velocity (MV), Darwin (D), spin-spin (SS), and orbit-orbit (OO) interactions used in the present work were derived starting from their representations in the laboratory coordinate frame and transforming them to the internal coordinate system described above.^{11,12} Due to the singlet states of both electrons and nuclei, the spin-orbit interaction and the interaction between the nuclear spins and the electron spin vanish. The MV, D, SS, and OO operators obtained after the transformation to the internal coordinate system for D₂ have the following form (in the Darwin term, the nuclear contributions proportional to the reciprocals of the squares of the nuclear masses are not included due to their very small contributions):

$$\hat{H}_{\text{MV}} = -\frac{1}{8} \left[\frac{1}{m_0^3} \left(\sum_{i=1}^3 \nabla_{\mathbf{r}_i} \right)^4 + \sum_{i=1}^3 \frac{1}{m_i^3} \nabla_{\mathbf{r}_i}^4 \right], \quad (2)$$

$$\hat{H}_{\text{D}} = -\frac{\pi}{2} \sum_{i=2}^3 \frac{q_i}{m_i^2} [q_0 \delta^3(r_i) + q_i \delta^3(r_{1i})] - \frac{\pi}{2} \sum_{i=2}^3 \sum_{j=2, j \neq i}^3 \frac{1}{m_i^2} q_i q_j \delta^3(r_{ij}), \quad (3)$$

$$\hat{H}_{\text{SS}} = 2\pi \frac{q_2 q_3}{m_2 m_3} \delta^3(r_{23}), \quad (4)$$

$$\hat{H}_{\text{OO}} = -\frac{1}{2} \sum_{i=1}^3 \sum_{j=1}^3 \frac{q_0 q_j}{m_0 m_j} \left[\frac{1}{r_j} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_j^3} \mathbf{r}_j \cdot (\mathbf{r}_j \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right] + \frac{1}{2} \sum_{i=1}^3 \sum_{j>i}^3 \frac{q_i q_j}{m_i m_j} \left[\frac{1}{r_{ij}} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} + \frac{1}{r_{ij}^3} \mathbf{r}_{ij} \cdot (\mathbf{r}_{ij} \cdot \nabla_{\mathbf{r}_i}) \nabla_{\mathbf{r}_j} \right]. \quad (5)$$

The total first-order relativistic correction is calculated for each state as the expectation value of $\alpha^2 \hat{H}_{\text{rel}}$ with the non-BO nonrelativistic wave function of that state, where

$$\hat{H}_{\text{rel}} = \hat{H}_{\text{MV}} + \hat{H}_{\text{D}} + \hat{H}_{\text{SS}} + \hat{H}_{\text{OO}}. \quad (6)$$

TABLE I. Total non-BO nonrelativistic energies and energies obtained by adding the leading α^2 relativistic corrections ($E_{\text{rel}} = E_{\text{nonrel}} + \alpha^2((\hat{H}_{\text{MV}}) + \langle \hat{H}_{\text{D}} \rangle + \langle \hat{H}_{\text{SS}} \rangle + \langle \hat{H}_{\text{OO}} \rangle)$) to the non-BO energy values for pure vibrational states of the D₂ molecule. The dissociation threshold (D + D) is given at the bottom. All values are in hartrees. Estimates of the remaining numerical uncertainty (due to finite size of the basis used) are shown in parenthesis.

v	E_{nonrel}	E_{rel}
0	-1.16716880921(5)	-1.16717971193(5)
1	-1.15352889591(50)	-1.15353971805(50)
2	-1.14043169537(100)	-1.14044244842(100)
3	-1.12786767622(100)	-1.12787837355(100)
4	-1.11582930519(200)	-1.11583995906(200)
5	-1.10431114712(200)	-1.10432177246(200)
6	-1.09331000143(300)	-1.09332060978(300)
7	-1.08282508802(300)	-1.08283569562(300)
8	-1.07285828595(300)	-1.07286890668(300)
9	-1.06341443481(500)	-1.06342508584(500)
10	-1.05450173416(500)	-1.05451243405(500)
11	-1.04613224297(500)	-1.04614300779(500)
12	-1.03832249181(500)	-1.03833334970(500)
13	-1.03109426783(500)	-1.03110523607(500)
14	-1.02447585067(500)	-1.02448695897(500)
15	-1.01850290707(1000)	-1.01851418581(1000)
16	-1.01322070784(1000)	-1.01323219244(1000)
17	-1.00868611256(1000)	-1.00869784448(1000)
18	-1.00497075927(3000)	-1.00498278591(3000)
19	-1.00216498142(3000)	-1.00217736172(3000)
20	-1.00038178995(3000)	-1.00039459041(3000)
21	-0.99973514848(10000)	-0.99974841717(10000)
D + D ^a	-0.99972763049	-0.99974094333

^aThe relativistic corrections for the D atom are calculated analytically using the exact nonrelativistic ground state wave function, $\psi(r_1) = \sqrt{(\mu^3/\pi)}e^{-\mu r_1}$, where $\mu = m_0 m_1 / (m_0 + m_1)$ is the reduced mass of the system (m_0 is the nuclear mass and m_1 is the electron mass). The corresponding expressions are $\langle \hat{H}_{\text{MV}} \rangle = -(5/8)((1/m_0^3) + (1/m_1^3))\mu^4$, $\langle \hat{H}_{\text{D}} \rangle = \mu^3/2m_1^2$, and $\langle \hat{H}_{\text{OO}} \rangle = -\mu^3/m_0 m_1$.

Due to the dependence of the relativistic operators and the non-BO wave function on the nuclear masses the total relativistic correction also depends on those masses.

As mentioned, in expanding the spatial parts the D₂ non-BO wave functions we use one-center, spherically symmetric ECGFs that include even non-negative powers of the internuclear distance, r_1 , as pre-exponential multipliers:⁶

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}], \quad (7)$$

where $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3\}'$ and prime ($'$) denotes the vector (matrix) transposition. The powers of m_k ranged from 0 to 250 in the present calculations.

The proper permutational symmetry is imposed on basis functions (7) before they are used to expand the wave function. As we are concerned with states which have singlet multiplicities for the electrons and the nuclei, each basis function is made symmetric with respect to the permutation of both the electrons and nuclei. Since the transformation between the laboratory and the internal coordinates is linear, the symmetrization operators, which originally are defined with respect to the laboratory coordinates, can be expressed in terms of the internal coordinates and directly applied to functions (7).⁶

TABLE II. Dissociation energies for the pure vibrational states of D₂ calculated using the nonrelativistic energies ($E_{\text{nonrel}}^{D+D} - E_{\text{nonrel}}^v$) and the energies obtained by adding relativistic α^2 corrections to the nonrelativistic energy values ($E_{\text{rel}}^{D+D} - E_{\text{rel}}^v$). All values are in cm⁻¹.

v	nonrel	rel
0	36 749.0910(0)	36 748.5620(2)
1	33 755.4760(0)	33 754.9294(2)
2	30 880.9728(1)	30 880.4110(2)
3	28 123.4893(2)	28 122.9153(3)
4	25 481.3723(3)	25 480.7887(5)
5	22 953.4288(5)	22 952.8389(5)
6	20 538.9564(5)	20 538.3628(5)
7	18 237.7839(10)	18 237.1901(10)
8	16 050.3236(10)	16 049.7328(10)
9	13 977.6379(20)	13 977.0537(20)
10	12 021.5262(20)	12 020.9527(20)
11	10 184.6352(30)	10 184.0760(30)
12	8470.5930(30)	8470.0542(30)
13	6884.1812(50)	6883.6666(50)
14	5431.6065(100)	5431.1227(100)
15	4120.6969(100)	4120.2505(100)
16	2961.3882(100)	2960.9869(100)
17	1966.1595(100)	1965.8126(100)
18	1150.7338(200)	1150.4515(200)
19	534.9367(200)	534.7320(200)
20	143.5714(200)	143.4590(200)
21	1.6500(400)	1.6403(400)

As mentioned, 10 000 ECGFs have been used in the present calculations to expand the wave function of each state. These functions have been extensively optimized using the variational energy minimization applied independently to each state. The ECGFs used in the calculations have to be square integrable. This automatically happens if A_k is represented in Cholesky-factored form, $A_k \equiv L_k L_k'$, with L_k being a lower triangular real matrix. Thus, the elements of the L_k matrices have been the nonlinear parameters optimized in the variational energy minimization. This optimization has been the most time consuming step of the calculations. We used the analytical gradient of the energy functional determined with respect to the L_k matrix elements to expedite the optimization process.

In the calculations of the lowest fifteen states the starting basis sets were taken from our previous calculations of H₂,²⁰ where both L_k and m_k parameters were optimized, and only the L_k parameters in those functions have been reoptimized to adjust the functions for the change of the nuclear masses. The justification of such an approach is based on the observation made by analyzing the H₂ basis sets which showed that, while for the first few states the m_k powers in the pre-exponential multipliers are mostly smaller numbers in the 0–250 range of numbers used in the calculations, the powers for higher states are approximately evenly distributed in the whole range of the allowed powers. That observation was also utilized in generating the initial basis sets for states 16–22 in the D₂ calculations. This was done by using the basis set of the 15-th state obtained after several optimization cycles to initiate the optimization of the basis set for the 16-th state, then using the

TABLE III. Some expectation values calculated for the pure vibrational states of the D_2 molecule with the non-BO nonrelativistic wave functions expanded in terms of 10 000 explicitly correlated Gaussians. $\langle r_{d-d} \rangle$, $\langle r_{d-e} \rangle$, and $\langle r_{e-e} \rangle$ denote the deuteron-deuteron, deuteron-electron, and electron-electron distances, respectively. All values are in a.u.

v	$\langle 1/r_{d-d} \rangle$	$\langle 1/r_{d-e} \rangle$	$\langle 1/r_{e-e} \rangle$	$\langle r_{d-d} \rangle$	$\langle r_{d-e} \rangle$	$\langle r_{e-e} \rangle$	$\langle r_{d-d}^2 \rangle$	$\langle r_{d-e}^2 \rangle$	$\langle r_{e-e}^2 \rangle$	$\langle \delta(\mathbf{r}_{d-e}) \rangle$	$\langle \delta(\mathbf{r}_{e-e}) \rangle$
1	0.703846	0.904959	0.581653	1.434562	1.567223	2.191855	2.077687	3.113364	5.754556	0.226936	0.016328
2	0.684680	0.890653	0.570874	1.502127	1.602852	2.236727	2.316156	3.265511	5.997527	0.222025	0.015565
3	0.665885	0.876702	0.560058	1.571586	1.639355	2.283476	2.571477	3.425548	6.255319	0.217340	0.014828
4	0.647400	0.863075	0.549166	1.643193	1.676851	2.332396	2.845420	3.594384	6.530145	0.212871	0.014110
5	0.629160	0.849743	0.538154	1.717255	1.715486	2.383841	3.140132	3.773132	6.824705	0.208612	0.013414
6	0.611092	0.836671	0.526971	1.794147	1.755439	2.438243	3.458252	3.963165	7.142316	0.204548	0.012727
7	0.593119	0.823824	0.515558	1.874335	1.796932	2.496127	3.803060	4.166195	7.487102	0.200661	0.012058
8	0.575154	0.811163	0.503847	1.958396	1.840244	2.558144	4.178687	4.384389	7.864235	0.196976	0.011392
9	0.557096	0.798643	0.491757	2.047064	1.885728	2.625111	4.590421	4.620525	8.280291	0.193449	0.010734
10	0.538831	0.786213	0.479190	2.141277	1.933838	2.698058	5.045138	4.878217	8.743744	0.190067	0.010078
11	0.520220	0.773812	0.466027	2.242258	1.985167	2.778314	5.551952	5.162256	9.265694	0.186849	0.009421
12	0.501095	0.761370	0.452120	2.351628	2.040503	2.867616	6.123199	5.479119	9.860968	0.183759	0.008762
13	0.481249	0.748795	0.437284	2.471590	2.100916	2.968288	6.776018	5.837786	10.549831	0.180824	0.008084
14	0.460419	0.735972	0.421282	2.605204	2.167893	3.083515	7.534925	6.251058	11.360775	0.177998	0.007395
15	0.438259	0.722753	0.403801	2.756873	2.243577	3.217807	8.436292	6.737855	12.335263	0.175311	0.006678
16	0.414306	0.708932	0.384415	2.933191	2.331170	3.377814	9.536668	7.327438	13.536448	0.172736	0.005929
17	0.387912	0.694220	0.362526	3.144567	2.435733	3.573883	10.929300	8.067789	15.066291	0.170254	0.005138
18	0.358112	0.678181	0.337240	3.408708	2.565866	3.823364	12.781204	9.044318	17.103538	0.167875	0.004292
19	0.323360	0.660102	0.307106	3.759177	2.737877	4.158757	15.429630	10.428375	20.001659	0.165568	0.003378
20	0.280825	0.638647	0.269432	4.271936	2.988720	4.652997	19.702832	12.638119	24.612108	0.163326	0.002371
21	0.223746	0.610540	0.217652	5.192368	3.438149	5.541074	28.620254	17.189291	33.987924	0.161132	0.001252
22	0.112976	0.556221	0.112436	9.854482	5.732263	10.072395	105.938573	55.958972	111.879887	0.159124	0.000104

16-th state basis for the 17-th state, and continuing this procedure until the last 22-th state was calculated.

The optimization of the basis set for each state has been carried out by cycling over all functions in the set multiple times and reoptimizing the parameters of only one function at a time. We found such an approach most effective for large basis sets. After the basis sets and the corresponding non-BO wave functions have been generated for all states the relativistic corrections were calculated. The sums of the nonrelativistic total energies and the relativistic corrections were subsequently used to calculate the D_2 dissociation energies corresponding to all 22 states.

III. THE RESULTS

In Table I we present the total nonrelativistic energies of all 22 pure vibrational states of D_2 obtained in the calculations. Based of the energy convergence patterns for the different states, we estimated numerical uncertainties of the energy values and these estimates are shown in the table in parenthesis next to the respective energies. As one can see, the convergence is noticeably better for the lower states than for the upper states because of the increasing number of the radial nodes, which becomes more difficult to describe with the same number of basis functions. In Table I we also show the total energies of the states with the leading α^2 relativistic corrections (MV+D+SS+OO) added to the nonrelativistic non-BO energies. The exact total nonrelativistic energy and the exact energy which includes the α^2 relativistic corrections are also shown in the table for two isolated D atoms. In Table II D_2 dissociation energies corresponding to the 22 states are presented. For each energy value we provide an esti-

mate of the error, which is due to the basis-set incompleteness. This incompleteness rises with the excitation level.

There is no doubt that the present non-BO calculations have been converged to a very high accuracy at the nonrelativistic level. Also, by explicitly including the finite nuclear masses in the calculations, the finite-mass effects (both adiabatic and nonadiabatic) are accounted for to high precision in the energy and the wave function. The finite-mass effects are also explicitly included in the calculations of the relativistic effects (the so-called recoil effects).

Finally, the nonrelativistic non-BO wave functions obtained for the 22 rotationless states of D_2 have been used to determine some commonly calculated expectation values. The results are shown in Table III. As expected the D_2 bond elongates as the vibrational excitation increases. The deuteron-electron and electron-electron expectation values elongate too. It is interesting to examine the expectation values for the highest bound vibrational state. This state is only bound by less than two wavenumbers. For this state the average internuclear distance is almost two times larger than for the next lower state. Same is true for the deuteron-electron and electron-electron average distances. These results indicate that, as this state is very close to the dissociation threshold, it may involve a higher level of coupling of the motions of the electrons and the nuclei. Such coupling is automatically included in our calculations.

IV. SUMMARY

In this work we present very accurate non-BO calculations of the whole pure vibrational spectrum of the D_2 molecule. A basis set of 10 000 explicitly correlated

Gaussian functions with extensively optimized exponential parameters is used in expanding the wave function of each state. The non-BO wave functions are used to evaluate the leading α^2 relativistic energy corrections. These corrections, along with the non-BO nonrelativistic energies, are then used to calculate the dissociation energy corresponding to each state. As the expected accuracy of these energies is very high, they may provide useful benchmark values for conventional calculations performed using the approach based on the potential energy cure.

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