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Non-Born-Oppenheimer calculations of the lowest vibrational energy of HD including relativistic corrections

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In this work we report variational calculations of the two lowest vibrational states of the HD molecule within the framework that does not assume the Born-Oppenheimer (BO) approximation. The nonrelativistic energies of the states were corrected for the relativistic effects of the order of α^2 (where $\alpha = \frac{1}{c}$), calculated as expectation values of the operators representing these effects with the nonrelativistic non-BO wave functions. The non-BO wave functions were expanded in terms of the one-center explicitly correlated Gaussian functions multiplied by even powers of the internuclear distance. The $v = 0 \rightarrow 1$ transition energy obtained in the calculations is compared with the previous calculations, as well as with the transition frequency obtained from the experimental spectra. The comparison shows the need to include corrections higher than second order in α to further improve the agreement between the theory and the experiment.

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I. INTRODUCTION

The quantum electrodynamics (QED) provides a general theoretical framework for calculating energies of stationary bound states of atoms and molecules with a very high accuracy [1,2]. Within this framework an effective approach was developed to account for the relativistic effects in light molecular systems based on the perturbation theory. The zeroth-order level in this approach is the nonrelativistic Schrödinger equation, and the perturbation Hamiltonian representing the relativistic effects is obtained based on the so-called nonrelativistic QED (NRQED) theory. A description of the NRQED theory and of the way the effective operators representing the relativistic effects are derived can be found in [2], as well as other sources. One should mention that the perturbation approach to account for the relativistic corrections can also be independently developed without using NRQED as it was shown by Bethe and Salpeter [3].

In the NRQED theory the corrections are quantities proportional to different powers of the fine-structure parameter α (where $\alpha = \frac{1}{c}$). In addition to the NRQED corrections one can also calculate corrections due to the structure of the nucleus and its polarizability. In the literature, the corrections proportional to α^2 are referred to as the leading relativistic corrections. The corrections proportional to higher powers of α are either pure QED corrections or higher-order relativistic corrections. In this work we calculated only the α^2 relativistic corrections that include corrections due to the mass-velocity (MV), Darwin (D), spin-spin (SS), and orbit-orbit (OO) interactions. The algorithms for calculating these corrections within the non-Born-Oppenheimer (BO) framework were presented recently [4,5].

Achieving high accuracy in calculations for diatomic molecular systems is more demanding than for atoms. This results from the fact that in the non-BO molecular calculations one needs to very accurately describe not only the electronic correlation effects but also the correlation effects due to the coupled motions of the electrons and the nuclei, as well as the nucleus-nucleus correlation effects. The latter effects are larger than the electron-electron correlation effects because the nuclei are much heavier and the probability of finding them near each other is much smaller than for electrons. To accurately describe the strong nuclear-nuclear correlation in a non-BO molecular calculation, one needs to use basis functions that effectively separate the nuclei. In our diatomic calculations this is accomplished by using explicitly correlated Gaussians multiplied by powers of the internuclear distance. We have shown in several works [6–8] that this basis set very effectively describes the correlation effects in systems consisting of particles with different masses interacting with Coulombic forces. The works also include our earlier non-BO calculations of the ground rovibrational states of the HD molecule performed with 512 explicitly correlated Gaussian functions [9]. The HD calculations shown in the present work are significantly more accurate than those presented in that earlier work.

There is a long history of using explicitly correlated Gaussians in electronic molecular calculations that goes back to the pioneering works of Boys [10] and Longstaff and Singer [11]. Later these functions were applied by several groups including Adamowicz and Sadlej [12] and Rychlewski and co-workers [13,14] in calculations of the correlation energy in small atomic and molecular system. A feature which makes the correlated Gaussians suitable for quantum-mechanical molecular calculations is the relative simplicity of the algorithms for calculating the Hamiltonian matrix elements with these functions.

We should add that in the non-BO calculations, the nonrelativistic Hamiltonian obtained after the separation of the motion of the center of mass is isotropic (i.e., rotationally

invariant) and the states of the system can be described by wave functions which transform according to the irreducible representations of the fully symmetric group of rotations. In particular the ground state or any rotationless state is described with a spherically symmetric *s*-type wave function. That is why we use spherically symmetric explicitly correlated functions in our calculations. Multiplying them by powers of the internuclear distance does not change this symmetry.

In recent works [4,5,15,16] we developed algorithms for calculating α^2 relativistic corrections for diatomic systems using non-BO wave functions expanded in terms of explicitly correlated Gaussians (ECGs) and the first-order perturbation theory. These algorithms are used in the present HD calculations. HD is a good model system for very accurate calculations because it has slight asymmetry of the electronic charge distribution that originates from the finite-mass effect. This effect is due to the fact that the electrons, on average, approach the deuterium nucleus slightly closer than the hydrogen nucleus because the electron reduce mass is slightly larger in the deuterium atom than in the hydrogen atom. The asymmetry in the electron behavior near the deuterium and hydrogen nuclei in HD results in an appearance of a slight dipole moment in this system. This dipole moment makes detection of the pure vibrational $v=0 \rightarrow 1$ transition possible in the experimental spectrum. The HD dipole moment was a subject of one of our previous calculations [17]. The dipole-moment value obtained there agreed very well with the experimental value of 0.000 345 a.u. [18].

The charge asymmetry of HD was considered with the use of the perturbation theory in the work of Blinder [19] in the early 1960s. The perturbation theory was also applied in the HD work of Kolos and Wolniewicz [20,21]. They represented the all-particle Hamiltonian as a sum of an operator symmetric with respect to the inversion of the nuclei and an antisymmetric perturbation. Then they calculated the first-order wave function as an expansion in terms of basis functions with the *u* symmetry. To solve the zero-order problem they used an approach previously applied to calculate all-particle vibronic energies for the H_2, D_2, and T_2 molecules where the wave functions were expanded in terms of basis functions with the *g* symmetry. Also, there were very accurate calculations performed on HD by Wolniewicz [22] where the HD rovibrational total and transition energies were determined using the conventional approach of solving the nuclear equation with the potential-energy curve obtained from the BO electronic calculations and corrected for the nonadiabatic, relativistic, and radiative corrections. In this work we compare our results with the results of Wolniewicz.

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 [6,7]). We also describe the procedure used to calculate the relativistic corrections. Next we describe the procedure used to obtain a better estimate of the lowest experimental pure vibrational transition frequency. The results obtained in the calculations and their comparison with the experimental results are presented in Sec. IV.

II. METHOD USED IN THE CALCULATIONS

The approach used in the present work in the HD calculations is based on the variational minimization of the total energy of the system 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 HD the internal Hamiltonian has the following form:

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

In Eq. (1) $q_0 = q_1 = 1$ are the charges of the nuclei (the proton and the deuteron) and $q_2 = q_3 = -1$ are the electron charges, $\mathbf{r}_i$, $i=1,2,3$, are the position vectors of the proton and the two electrons with respect to the deuteron (placed in the center of the internal coordinate system and called the "reference particle"), r_i are their lengths, $r_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$, $m_0 = 3670.482\,965\,4 m_e$ and $m_1 = 1836.152\,672\,47 m_e$ [23] are the masses of the deuteron and the proton, respectively, $m_2 = m_3 = m_e = 1$ are the electron masses, and $\mu_i = m_0 m_i/(m_0 + m_i)$ is the reduced mass of particle i. The internal Hamiltonian (1) describes three "pseudoparticles" with charges equal to the charges of the original particles but with masses changed to the reduced masses. The pseudoparticles move in the central potential of the charge of the reference particle. In Hamiltonian (1) the motions of the three pseudoparticles are coupled through the Coulomb interactions and through the so-called mass-polarization term, $-\frac{1}{2}\sum_{i=1}^{3}\sum_{j\neq i}^{3}\frac{1}{m_0}\nabla_{\mathbf{r}_i}\cdot\nabla_{\mathbf{r}_j}$.

To calculate the relativistic corrections of the order of α^2 we use the Breit-Pauli Hamiltonian and the first-order perturbation theory. This approach has been used by others in very accurate calculations of light atoms and molecules [24–26]. One should also mention the work showing that the two-electron correlated Gaussians (Gaussian geminals) are capable of producing good results when the Breit-Pauli Hamiltonian is used to represent the relativistic affects [27]. We should mention that there is an alternative approach for calculating the relativistic corrections based on the direct perturbation theory [28]. The approach avoids the problem with the singularities which are present in the Breit-Pauli Hamiltonian, and it is useful when higher-order relativistic corrections are calculated.

In the present calculations we start with the respective Breit-Pauli operators representing the MV, D, SS, and OO interactions in the laboratory coordinate frame, and we transform them to the internal coordinate system of the nine coordinates, $\mathbf{r}_i$, $i=1,2,3$. More details of this transformation for the MV, D, and OO corrections can be found in [4,5]. The transformed MV, D, SS, and OO Hamiltonians have the following form:

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

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

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

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

We should mention that the spin-orbit interactions are zero for HD due to the singlet multiplicity of the electrons and the zero total angular momentum of the states we consider in this work. Also, the spin-spin interaction between the proton and the electrons is zero because of the electron singlet multiplicity.

The total relativistic correction was calculated for each state as the expectation value of the Hamiltonian $\hat{H}_{rel}$ representing all four relativistic corrections,

$$\hat{H}_{rel} = \hat{H}_{MV} + \hat{H}_D + \hat{H}_{SS} + \hat{H}_{OO} \tag{6}$$

with the non-BO wave function.

The spatial part of the HD non-BO wave functions of the pure rotationless vibrational states are expanded in terms of the one-center spherically symmetric ECGs that included pre-exponential multipliers consisting of the internuclear distance, r_1, raised to a non-negative even power, m_k. These are the same functions as those used before in our non-BO calculations of other diatomic systems [8]. The functions have the following form:

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

where $\mathbf{r} = \{\mathbf{r}'_1, \mathbf{r}'_2, \mathbf{r}'_3\}'$ and $'$ denotes the vector (matrix) transposition. Before the functions in Eq. (7) are used in expanding an HD wave function, they are symmetrized with respect to the electron labels. Since the transformation between the laboratory and the internal coordinates is linear, the symmetrization operator, which originally is defined with respect to the laboratory coordinates, can be expressed in terms of the internal coordinates and directly applied to function (7).

In our previous calculations we have demonstrated that the basis functions in Eq. (7) are very effective in describing nonadiabatic zero angular-momentum states of diatomic systems with σ electrons. The $r_1^{m_k}$ factors in function (7) generate nodes in the wave function in terms of the r_1 coordinate and very effectively describe the nucleus-nucleus correlation effects. We refer the reader for more information on the Hamiltonian transformation and the selection of the basis functions for diatomic non-BO calculations to our recent reviews [6,7]. The derivation of the algorithms of the matrix elements with the $\hat{H}_{MV}$, $\hat{H}_D$, $\hat{H}_{SS}$, and $\hat{H}_{OO}$ operators were described in [4,5].

In the present work we used the standard variational method applied separately to each state. The minimization of the Rayleigh quotient with respect to the linear-expansion coefficients, $\{c_k\}$, the Gaussian exponential parameters, $\{A_k\}$, and the pre-exponential powers, $\{m_k\}$, and generating the wave functions

$$E = \min \frac{c' H(\{m_k\}, \{A_k\}) c}{c' S(\{m_k\}, \{A_k\}) c} \tag{8}$$

have been the most time-consuming part of the calculations. In the minimization of functional (8) with respect to the Gaussian exponential parameters, we used the analytical energy gradient which greatly accelerated the process of the wave-function optimization. Also, in order to avoid restricting the elements of the A_k matrix to make it positive definite, we used the Cholesky-factored form of A_k, $A_k \equiv L_k L'_k$, where L_k is a lower triangular matrix. With such a representation of A_k, this matrix is automatically positive definite for any real values of the L_k matrix elements. In the calculation the L_k matrix elements replaced the elements of A_k as the optimization variables. The analytical energy gradient is calculated with respect to these elements. The pre-exponential powers, m_k, in this work ranged from 0 to 250, and all the powers were partially optimized for each state.

The calculations concerned the two lowest pure vibrational states of HD. As mentioned, the maximum number of basis functions used for each state was 10 000. To generate this number of functions the basis set was grown from a small randomly selected set of a few dozen functions using a multistep procedure. When the basis set was relatively small (less than 100 functions) each step involved adding a group of ten functions, one function at a time, optimizing their exponential parameters using the gradient-based minimization approach, and when the addition was finished, reoptimizing the whole basis set using the same gradient-based approach. In this reoptimization the parameters of all basis functions were simultaneously adjusted. When the number of basis functions exceeded 100, the number of functions added in each step was increased to 20 and the reoptimization of the whole set at the end of each step was done by adjusting the parameters of only one function at a time. When the basis set reached the level of 10 000 functions, the cyclic one-function-at-a-time optimization was repeated multiple times to get the lowest possible energy.

After the non-BO nonrelivistic wave functions were generated for the two states, we used them to calculate the relativistic corrections. The nonrelativistic energies corrected for the relativistic effects were used to calculate the transition frequencies. The non-BO wave functions, $\Psi(\mathbf{r})$, were also used to calculate the one-particle (i.e., one-pseudoparticle) density associated with pseudoparticle 1 (i.e., pseudoproton) using the following formula [29]:

$$g(\xi) = \langle \Psi(\mathbf{r}) | \delta(\mathbf{r}_1 - \xi) | \Psi(\mathbf{r}) \rangle = \int_{-\infty}^{\infty} |\Psi(\xi, \mathbf{r}_2, \mathbf{r}_3)|^2 d\mathbf{r}_2 d\mathbf{r}_3,$$
$$\tag{9}$$

where $\delta(\mathbf{r}_1 - \xi)$ is the three-dimensional Dirac delta function. For HD the pseudoparticle 1 density is equivalent to the deuteron-proton correlation function. As in the non-BO calculation the molecular structural parameters (bond lengths and bond angles) are obtained as expectation values of these

TABLE I. Dunham's spectral parameters (cm^{-1}) for deuterium hydride ^{1}H^{2}H fitted to the band $v=0 \rightarrow 1$.

Y_{ij}	$v=0 \rightarrow 1$
Y_{10}	3632.1595(17)
Y_{11}	$-1.92865(85)$
$Y_{12} \times 10^4$	1.430636(68)
Y_{01}	45.62989(69)
$Y_{02} \times 10^2$	$-2.6088(41)$
$Y_{03} \times 10^5$	2.50(40)
$Y_{04} \times 10^8$	$-4.8(34)$
$\hat{\sigma}$	1.79
$J_{\min} - J_{\max}$	0–5
Lines	32
$\nu_{0 \rightarrow 1}$	3632.1595(17)

parameters with the non-BO wave function. There is no definite molecular structure that comes out from the calculation such as the structure one gets from a BO calculation. In such a situation the density plots provide complementary information to the expectation values of the structural parameters. For HD the only parameter that characterizes its structure is the internuclear distance. In addition to calculating the expectation value of this distance in this work we also calculated the deuteron-proton correlation function.

III. ESTIMATION OF PURE VIBRATIONAL $v=0 \rightarrow 1$ TRANSITION OF HD FROM THE AVAILABLE ROTATION-VIBRATIONAL SPECTRA

The rotation-vibrational spectrum of deuterium hydride is very weak as the spectral transitions arise only from the breakdown of the Born-Oppenheimer approximation and from the appearance of a very small dipole moment in this system [30]. The spectral lines of HD were first observed by Herzberg [31] in 1950. In 1960 the $v=0 \rightarrow 2$ overtone band

of HD was analyzed by Durie and Herzberg [32].

In this work we determined the frequency of the experimental pure vibrational transition ($J=0$), $v=0 \rightarrow 1$, of HD by making use of the 32 spectral lines (including duplicated lines measured with different precision) reported in Refs. [30,33–37]. The spectra in those works were obtained by employing different techniques. For example, Ref. [30] used the photoacoustic measurements at a low pressure with a shorter absorption path.

We estimated the $\nu_{0 \rightarrow 1}$ frequency by fitting the spectral line positions to the energy formula of Dunham [38],

$$E_{vJ} = \sum_{i,j} Y_{ij} \left(v + \frac{1}{2} \right)^i [J(J+1)]^j, \qquad (10)$$

where $v=0,1,2,\ldots$ and $J=0,1,2,\ldots$ denote the vibrational and rotational quantum numbers. Then the frequency of the $\nu_{0 \rightarrow 1}$ vibrational transition was directly obtained from the relation

$$\nu_{0 \rightarrow 1} = Y_{10} \text{ cm}^{-1}, \qquad (11)$$

derived under the assumption that the higher-order vibrational parameters, Y_{20}, Y_{30}, etc., are negligible.

The calculations were performed using a weighted nonlinear least-squares routine with weights taken as inverse squares of the uncertainties of the experimental data, u_i, ranging from 0.01 to 0.001 cm^{-1} [33–37,39]. To obtain the best set of Dunham's parameters, Y_{ij}, from the experimental spectral transitions, we used the following in the fitting procedure: the minimum number of fitted parameters consistent with the minimum values of the normalized standard deviation, $\hat{\sigma}$, and the standard deviation, σ; optimal values of the estimated standard error, σ_i, of each fitted parameter and of the coupling coefficient describing the correlation between each pair of the parameters. The results of the calculation are presented in Table I.

Even though the parameter $Y_{04} \times 10^8 = -4.8(34)$ is not evaluated as accurately as the other parameters, its absence from the fit results in a less accurate spectral reproduction at

TABLE II. The convergence of the total nonrelativistic non-BO energies (E_{nrel}) of the two lowest vibrational states of the HD molecule with the number of basis functions (in hartree).

No. of basis functions	$E_{\text{nrel}}(v=0)$	$E_{\text{nrel}}(v=1)$
1000	-1.1654717568	-1.1489218639
2000	-1.1654718954	-1.1489224960
3000	-1.1654719119	-1.1489225611
4000	-1.1654719166	-1.1489225754
5000	-1.1654719185	-1.1489225810
6000	-1.1654719197	-1.1489225845
7000	-1.1654719204	-1.1489225863
8000	-1.1654719211	-1.1489225878
9000	-1.1654719216	-1.1489225887
10000[a]	$-1.1654719219(20)$	$-1.1489225894(30)$
10000[b]	$-1.1654719220(20)$	$-1.1489225895(30)$

[a]Uncertainties of the calculated energies are shown in parenthesis.
[b]Results obtained by performing several additional cyclic optimizations of the nonlinear parameters.

TABLE III. Relativistic corrections of the order of α^2 (in hartree) to the non-BO pure vibrational energies of the two lowest vibrational states of the HD molecule and the contribution of the relativistic correction to the transitions energy.

No. of basis functions	$\langle \hat{H}_{MV}+\hat{H}_D+\hat{H}_{SS}\rangle$	$\langle \hat{H}_{OO}\rangle$	Total relativistic correction
		$v=0$	
1000	-8.348598×10^{-6}	-2.529434×10^{-6}	-1.087803×10^{-5}
2000	-8.357285×10^{-6}	-2.529410×10^{-6}	-1.088669×10^{-5}
3000	-8.357542×10^{-6}	-2.529411×10^{-6}	-1.088695×10^{-5}
4000	-8.360602×10^{-6}	-2.529409×10^{-6}	-1.089001×10^{-5}
5000	-8.361319×10^{-6}	-2.529407×10^{-6}	-1.089073×10^{-5}
6000	-8.361684×10^{-6}	-2.529407×10^{-6}	-1.089109×10^{-5}
7000	-8.362055×10^{-6}	-2.529407×10^{-6}	-1.089146×10^{-5}
8000	-8.363093×10^{-6}	-2.529407×10^{-6}	-1.089250×10^{-5}
9000	-8.363099×10^{-6}	-2.529407×10^{-6}	-1.089251×10^{-5}
10000	-8.363647×10^{-6}	-2.529406×10^{-6}	-1.089305×10^{-5}
10000[a]	-8.363665×10^{-6}	-2.529406×10^{-6}	-1.089307×10^{-5}
		$v=1$	
1000	-8.367559×10^{-6}	-2.417959×10^{-6}	-1.078552×10^{-5}
2000	-8.367752×10^{-6}	-2.417927×10^{-6}	-1.078568×10^{-5}
3000	-8.374977×10^{-6}	-2.417911×10^{-6}	-1.079289×10^{-5}
4000	-8.373074×10^{-6}	-2.417910×10^{-6}	-1.079098×10^{-5}
5000	-8.374112×10^{-6}	-2.417905×10^{-6}	-1.079202×10^{-5}
6000	-8.375121×10^{-6}	-2.417901×10^{-6}	-1.079302×10^{-5}
7000	-8.375079×10^{-6}	-2.417901×10^{-6}	-1.079298×10^{-5}
8000	-8.376297×10^{-6}	-2.417900×10^{-6}	-1.079420×10^{-5}
9000	-8.376353×10^{-6}	-2.417900×10^{-6}	-1.079425×10^{-5}
10000[a]	-8.376841×10^{-6}	-2.417900×10^{-6}	-1.079474×10^{-5}
10000[a]	-8.376838×10^{-6}	-2.417899×10^{-6}	-1.079474×10^{-5}

[a]Results obtained by performing several additional cyclic optimizations of the nonlinear parameters.

$\hat{\sigma}=1.82$. With that, the corresponding frequency becomes $\nu_{0\rightarrow 1}=3632.1607(15)$ cm^{-1}. Including this term gives the $\nu_{0\rightarrow 1}$ frequency of $3632.1595(17)$ cm^{-1} that agrees very well with the somewhat less accurate result of Rich *et al.* [33] of $\nu_{0\rightarrow 1}=3632.159(6)$.

IV. RESULTS

In Table II we present the total nonrelativistic energies for the two lowest vibrational states obtained in the calculations. For each state the energy values obtained with basis sets ranging in size from 1000 to 10 000 in increments of 1000 are shown. As one can see, a very good convergence has been achieved for each state. The ninth significant digit is essentially converged. The ground $v=0$ state converges slightly better than the first-excited $v=1$ state. The additional optimization cycles for the 10 000-term basis lowered the energy of the ground state by 0.8×10^{-10} hartree and the first-excited state by 1.3×10^{-10} hartree.

In Table III we show the convergence of the $\langle \hat{H}_D+\hat{H}_D+\hat{H}_D\rangle$ and $\langle \hat{H}_{OO}\rangle$ contributions to the α^2 relativistic correction and their sum. We also provide uncertainty estimates of these corrections.

The $v=0\rightarrow 1$ transition frequency calculated with different numbers of basis functions are presented in Table IV. We show the results obtained with and without the relativistic corrections. The frequencies are compared with the frequency obtained by Wolniewicz [22]. The approach used by Wolniewicz was based on the Born-Oppenheimer approximation that produced the zero-order wave function which was subsequently used to calculate finite-mass corrections (adiabatic and nonadiabatic) and the relativistic and radiative corrections. The potential-energy curve, which included those corrections, was then used to determine the vibrational energies. Table IV also includes a comparison with the experimental frequency. Wolniewicz concluded his work by saying that the most important source of errors in his calculations was a result of the nonadiabatic corrections. Even though his final transition energy is in excellent agreement with the experiment, in view of his concluding statement, the agreement could have been somewhat fortuitous. As the present non-BO calculations have been converged to a very high accuracy at the nonrelativistic level and the finite-mass effects (both adiabatic and nonadiabatic) have been explicitly accounted for in the variational energy and the wave function, these effects are automatically included in our results to

TABLE IV. Convergence of the HD lowest pure vibrational transition frequency calculated using the nonrelativistic ($E_{v=1}^{nr} - E_{v=0}^{nr}$) and relativistic ($E_{rel}^{v=1} - E_{rel}^{v=0}$) total energies.

No. of basis functions	$E_{nr}^{v=1} - E_{nr}^{v=0}$	$E_{rel}^{v=1} - E_{rel}^{v=0}$
1000	3632.2817	3632.3020
2000	3632.1733	3632.1955
3000	3632.1627	3632.1833
4000	3632.1606	3632.1823
5000	3632.1597	3632.1814
6000	3632.1592	3632.1808
7000	3632.1590	3632.1806
8000	3632.1588	3632.1804
9000	3632.1587	3632.1803
10000[a]	3632.1587(4)	3632.1802(4)
10000[b]	3632.1587(4)	3632.1802(4)
Wolniewicz [22]		3632.154
Experiment[c]		3632.1595

[a]Uncertainties of the calculated transition energies are shown in parenthesis.
[b]Results obtained by performing several additional cyclic optimizations of the nonlinear parameters.
[c]This work.

TABLE V. Some expectation values calculated for the $v=0$ and $v=1$ vibrational states of the HD molecule with the wave functions expanded in terms of 10 000 Gaussian basis functions. All values are in a.u.

Expectation value	$v=0$	$v=1$
$\langle r_1^{-1} \rangle$	0.701604	0.678247
$\langle r_{12}^{-1} \rangle$	0.903137	0.885723
$\langle r_2^{-1} \rangle$	0.903333	0.885916
$\langle r_{23}^{-1} \rangle$	0.580391	0.567188
$\langle r_1 \rangle$	1.442229	1.525466
$\langle r_{12} \rangle$	1.571475	1.615340
$\langle r_2 \rangle$	1.571185	1.615045
$\langle r_{23} \rangle$	2.196970	2.252414
$\langle r_1^2 \rangle$	2.104322	2.400880
$\langle r_{12}^2 \rangle$	3.131202	3.319670
$\langle r_2^2 \rangle$	3.130094	3.318524
$\langle r_{23}^2 \rangle$	5.781954	6.083447
$\langle \delta(\mathbf{r}_1) \rangle$	1.713771×10^{-12}	8.119417×10^{-12}
$\langle \delta(\mathbf{r}_{12}) \rangle$	0.225891	0.219983
$\langle \delta(\mathbf{r}_2) \rangle$	0.226371	0.220413
$\langle \delta(\mathbf{r}_{23}) \rangle$	1.623499×10^{-2}	1.531738×10^{-2}

a very high precision. The finite-mass effects are also explicitly included in the calculations of the relativistic effects. Therefore we did not have to resort to the perturbation theory to calculate corrections due to these effects (the so-called recoil corrections) as done in the conventional approach. Examples of using the conventional approach include recent work of Pachucki and Komasa [40] and Jaquet and Kutzelnigg [41]. We believe that our transition energies are converged to within 0.001 cm^{-1}. This leaves the quantum electrodynamics (QED) corrections as the only source of error in our determination of the $v=0 \rightarrow 1$ transition frequency.

In the last step the nonrelativistic wave functions obtained for the $v=0$ and $v=1$ states were used to determine some commonly calculated expectation values. The values are shown in Table V. They are particularly interesting for HD because they show the slight asymmetry in the electronic charge distribution induced by the asymmetry of the nuclear masses. For example, let us compare the expectation values of the deuteron-electron distance, $\langle r_2 \rangle$, and the proton-electron distance, $\langle r_{12} \rangle$ for the two states. As one can see the latter values are slightly larger than the former ones, indicating that in both states the electrons are, on average, closer to the deuteron than to the proton. This effect is also manifested in the contact terms, i.e., the $\langle \delta(\mathbf{r}_{12}) \rangle$ and $\langle \delta(\mathbf{r}_2) \rangle$ expectation values. Again the values related to the deuteron for both states are slightly larger than the values related to the proton.

Finally, we found it interesting to show proton-deuteron correlation functions (the pseudoproton densities) for the two states considered in this work. Plots of these densities are shown in Fig. 1. As noted, as the internal Hamiltonian (1) is rotationally invariant, the wave functions for rotationless vibrational states are spherically symmetric with respect to the center of the internal coordinate system. Hence, the

pseudoproton densities for these states are also fully symmetric functions. To emphasize this, we plotted the densities calculated for a two-dimensional (2D) cross-section cutting through the center of the internal coordinate system. As expected, the symmetric 2D density for the $v=0$ state (the ground state) has a maximum value on a ring with the radius equal to about the average value of the HD internuclear dis-
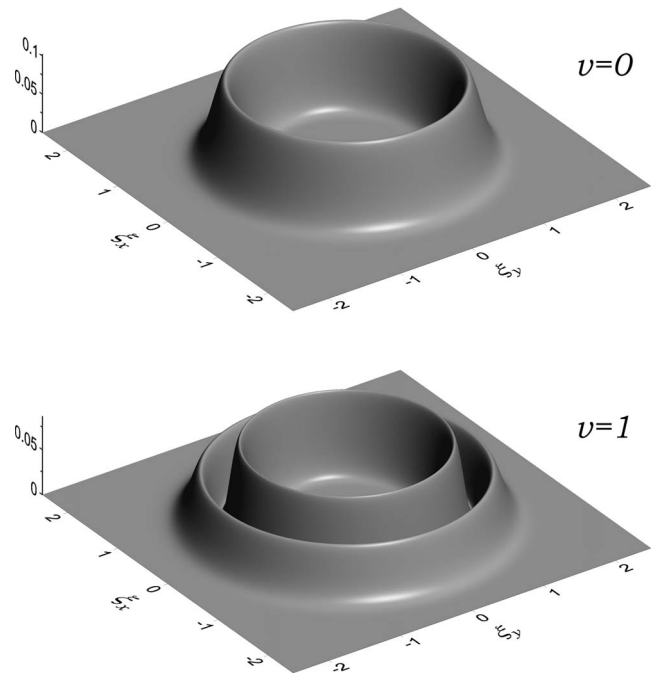

FIG. 1. Deuteron-proton correlation functions for the $v=0$ and $v=1$ pure vibrational states of the HD molecule.

tance. For the $v=1$ state, the 2D density shows maxima on two rings corresponding to the two extrema of the wave function of the first-excited vibrational state.

To describe the radial oscillations of the $v=0$ and $v=1$ wave functions, the Gaussians in the basis set are multiplied by powers of the internuclear distance r_1. The different radial behaviors of the two wave functions require different distributions of the powers. We found it interesting to show how different these distributions are for the two states. This is shown in Fig. 2. As one notices, the powers, which, as mentioned before, range from 0 to 250, are, on average, smaller for the ground state than for the first-excited state. Also, the powers are more evenly distributed for the excited states than for the ground state. This is because for the excited state they need to describe two radial maxima and only one for the ground state.

V. SUMMARY

In this work we presented accurate calculations for the two lowest pure vibrational states of the HD molecule using the non-BO framework and explicitly correlated Gaussian functions. The non-BO wave functions were used to evaluate the α^2 relativistic corrections. Even with adding these corrections, the $v=0 \rightarrow 1$ transition frequency still differs from the experimental value by about 0.02 cm^{-1}. To further increase the accuracy of the calculations one needs to include the lowest-order QED corrections, as well as corrections due to the finite sizes of the nuclei and due to their polarizabilities. Our future effort will go in this direction. The future work will also include calculations of all remaining 16 pure vibrational states of HD.

The high accuracy demands of the calculations required that each of the two states is considered separately. Thus a separate basis set of explicitly correlated Gaussians was generated for each state. Since both states correspond to the zero total angular momentum their wave functions were expanded in terms of Gaussians with the s symmetry. Treatment of states with nonzero total angular momentum requires multiplying the Gaussians by angular factors. Work in deriving algorithms for calculating matrix elements of the Hamiltonian and the energy gradient with such functions is currently in progress in our laboratory.
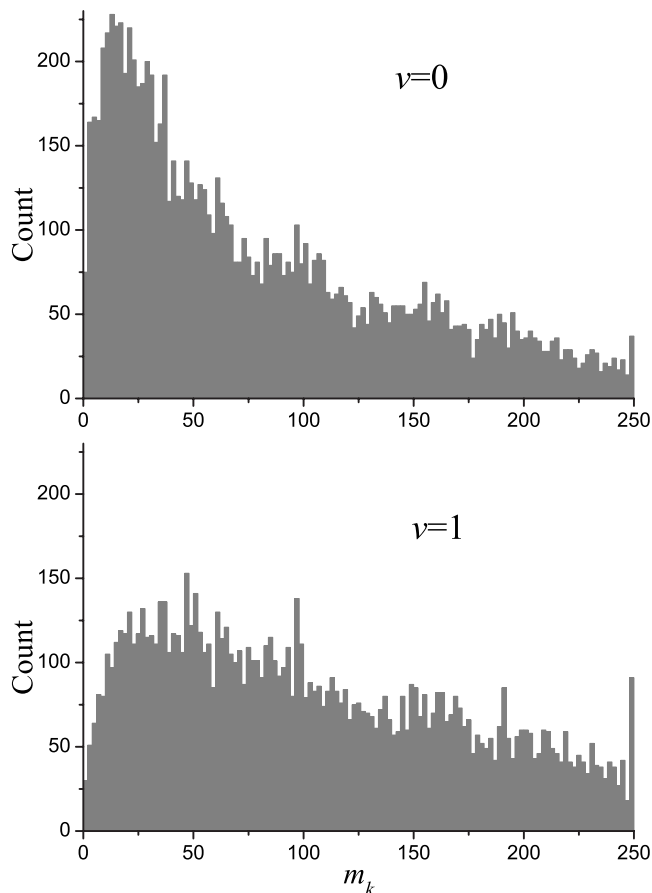

FIG. 2. Distributions of the r_1 powers, m_k, in the 10 000-term basis sets obtained for the $v=0$ and $v=1$ pure vibrational states of the HD molecule.

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