Charge asymmetry and relativistic corrections in pure vibrational states of the HD$^+$ ion

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In this work we present very accurate quantum-mechanical calculations of all bound pure vibrational states of the HD$^+$ ion performed without the Born-Oppenheimer (BO) approximation. All three particles forming the system are treated on equal footing. The approach involves separating the center-of-mass motion from the laboratory-frame nonrelativistic Hamiltonian and expending the wave function of each considered state in terms of all-particle explicitly correlated Gaussian functions. The Gaussian exponential parameters are variationally optimized with the aid of the analytical energy gradient calculated with respect to these parameters. For each state the leading relativistic corrections are calculated as expectation values of the corresponding operators with the non-BO wave function of the state. The non-BO approach allows us to directly describe the charge asymmetry in HD$^+$ which is due to the nuclear-mass asymmetry. The effect increases with the vibrational excitation and affects the values of the relativistic corrections. This phenomenon is the focus of the present study.

I. INTRODUCTION

The idea of performing quantum calculations on molecular systems without assuming the Born-Oppenheimer approximation regarding the separability of the motions of electrons and nuclei is not new. These types of calculations have been done since the very early stage of the development of quantum chemistry and have continued till the present day [1–6]. The calculations have revealed the importance of the nonadiabatic effects in the calculations of the spectra and other properties of molecules and molecular ions.

The HD$^+$ ion is good model system to study how the nonadiabatic effects affect the properties of a molecular system. This is because as the vibrational excitation increases, the charge asymmetry resulting from the electron being positioned closer to the deuteron than to the proton increases. This asymmetry effect can only be described in quantum-mechanical calculations if the Born-Oppenheimer (BO) approximation is not assumed. The charge asymmetry increases to the point that in the two top vibrational states the electron is almost entirely localized at the deuteron [7]. Thus the character of the bond changes from being predominantly covalent in the lowest vibrational states to ionic in the highest states.

There are 23 bound pure vibrational states of HD$^+$. In our previous work we calculated the energies of these states employing a non-BO approach and all-particle explicitly correlated Gaussian (ECG) functions. 2000 ECGs were used for each state except for the top one ($v = 22$) for which 4000 ECGs were used. The non-BO wave functions were employed to calculate the mass-velocity and Darwin relativistic corrections, which account for the relativistic effects not only associated with the electronic motions, but also the motion of the nuclei. In the present non-BO calculations of the HD$^+$ pure vibrational states the number of Gaussians in the basis set for each state is doubled. This allows for achieving much better energy convergence. Also the orbit-orbit (OO) relativistic interactions are accounted for in the leading relativistic correction. With these, the present results are significantly more accurate than those obtained before. They can serve as benchmark values for

other calculations, particularly those performed with methods based on the BO approximation.

In recent paper [8] we used the ECG basis sets generated in Ref. [7] for the pure vibrational states of HD$^+$ to calculate the leading relativistic corrections for these states. We also examined how the charge asymmetry affects these corrections. In the present work a similar analysis is also performed based on the new results which are much improved in comparison with the results of Ref. [7].

II. HAMILTONIAN

The conventional nonrelativistic quantum-mechanical calculations of atomic and molecular systems are performed assuming the Born-Oppenheimer (BO) approximation. Thus, the potential energy surface (PES) is first generated by solving the electronic Schrödinger equation and then this PES is used as the potential in the Schrödinger equation describing the motion of the nuclei. By solving this equation the energies and the wave functions of the rovibrational states are determined. Subsequently, the accuracy of the results (energies) can be improved by including adiabatic and nonadiabatic corrections. A more direct and potentially more accurate and rigorous (and perhaps also more interesting) approach is not to assume the BO approximation and to treat all particles forming the system on equal footing. In such an approach the coupling of the motions of the light particles (electrons, positrons) and heavy particles (nuclei) is not neglected or treated approximately. The non-BO approach, besides being conceptually appealing, can provide results which are more accurate than those obtained with a method based on the BO approximation. The effort to generate very accurate results in molecular calculations is motivated by the constantly increasing accuracy of the experimental techniques used to measure the molecular spectra. These measurements are starting to reach accuracy of sub 0.0001 cm^{-1} which is very hard to achieve in theoretical calculations based on first principles.

The method for very accurate atomic and molecular calculations developed by the Adamowicz group in recent years [9–16] is based on equal treatment of all N particles forming

the system. The approach starts with the general laboratory-frame nonrelativistic Hamiltonian for the considered molecule (or atom), which consists of N quantum particles with masses M_i and charges Q_i ($i = 1, \ldots, N$). Let vectors $\mathbf{R}_i$ describe the positions of the particles in a laboratory coordinate frame and vectors $\mathbf{P}_i$ the corresponding linear momenta:

$$\mathbf{R} = \begin{bmatrix} \mathbf{R_1} \\ \mathbf{R_2} \\ \cdots \\ \mathbf{R_N} \end{bmatrix} = \begin{bmatrix} X_1 \\ Y_1 \\ Z_1 \\ \vdots \\ Z_N \end{bmatrix}, \quad \mathbf{P} = \begin{bmatrix} \mathbf{P_1} \\ \mathbf{P_2} \\ \cdots \\ \mathbf{P_N} \end{bmatrix} = \begin{bmatrix} P_{x1} \\ P_{y1} \\ P_{z1} \\ \vdots \\ P_{zN} \end{bmatrix}. \quad (1)$$

The nonrelativistic laboratory-frame Hamiltonian of the system is

$$H_{\mathrm{nr}}(\mathbf{R}) = \sum_{i=1}^{N} \frac{\mathbf{P}_i^2}{2M_i} + \sum_{i=1}^{N} \sum_{j>i}^{N} \frac{Q_i Q_j}{\|\mathbf{R}_i - \mathbf{R}_j\|}. \quad (2)$$

Next, the $3N$-dimensional problem represented by the above Hamiltonian is reduced to a $(3N - 3)$-dimensional problem by eliminating from the laboratory-frame Hamiltonian the center-of-mass motion. This elimination is achieved by transforming the Hamiltonian to a new coordinate system, whose first three coordinates, $\mathbf{r}_0$, are the coordinates of the center of mass in the laboratory coordinate frame and the remaining $3N - 3$ coordinates are internal coordinates. The internal coordinates, $\mathbf{r}_i, i = 1, \ldots, N - 1$, are coordinates in a Cartesian coordinate system whose center is placed at a selected reference particle (usually the heaviest one). Let us denote $N - 1$ by n. The application of the coordinate transformation to the laboratory-frame total Hamiltonian (2) allows for separating out the operator representing the kinetic energy of the center-of-mass motion from the internal Hamiltonian:

$$H_{\mathrm{nr}}^{\mathrm{tot}}(\mathbf{r}_0, \mathbf{r}) = \left(-\frac{1}{2} \frac{1}{M_{\mathrm{tot}}} \nabla_{\mathbf{r}_0}^2 \right) + \left(-\frac{1}{2} \sum_{i}^{n} \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 \right.$$
$$\left. -\frac{1}{2} \sum_{i \neq j}^{n} \frac{1}{m_0} \nabla_{\mathbf{r}_i} \nabla_{\mathbf{r}_j} + \sum_{i<j}^{n} \frac{q_i q_j}{r_{ij}} + \sum_{i=1}^{n} \frac{q_0 q_i}{r_i} \right), \quad (3)$$

where $q_i = Q_{i+1}$, $\mu_i = \frac{m_0 m_i}{m_0 + m_i}$ are the reduced masses, M_{tot} is the total mass of the system, m_0 is the mass of the reference particle, $m_i = M_{i+1}$, $\nabla_{\mathbf{r}_i}$ is the gradient vector expressed in terms of the x_i, y_i, z_i coordinates of vector $\mathbf{r}_i$, $r_{ij} = \|\mathbf{r}_i - \mathbf{r}_j\| = \|\mathbf{R}_{i+1} - \mathbf{R}_{j+1}\|$, and $r_{0i} \equiv r_i = \|\mathbf{r}_i\| = \|\mathbf{R}_{i+1} - \mathbf{R}_1\|$. One can call the particles described by the above Hamiltonian "pseudoparticles" because, even though they have the same charges as the original particles, their masses are not the original masses but the reduced masses. The separation of the total nonrelativistic laboratory-frame Hamiltonian into the operator representing the kinetic energy of the center-of-mass motion, $H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0)$, and the internal Hamiltonian, $H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r})$, is rigorous:

$$H_{\mathrm{nr}}^{\mathrm{tot}}(\mathbf{r}_0, \mathbf{r}) = H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0) + H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r}). \quad (4)$$

The sum of $H_{\mathrm{nr}}^{\mathrm{cm}}(\mathbf{r}_0)$ and $H_{\mathrm{nr}}^{\mathrm{int}}(\mathbf{r})$ provides a complete description of the state of all particles in space. As in this work we are

only concerned with the internal bound states of the system, the eigenvalues and eigenfunctions of the internal Hamiltonian are calculated. The internal Hamiltonian can be viewed as describing a system of n pseudoparticles with the masses equal to reduced masses μ_i and charges q_i ($i = 1, \ldots, n$) moving in the central field of the charge of the reference particle, q_0. The pseudoparticles interact with each other by the Coulombic potential and additionally their motions are coupled through the mass-polarization terms, $-\frac{1}{2} \sum_{i \neq j}^{n} \frac{1}{m_0} \nabla_{\mathbf{r}_i} \nabla_{\mathbf{r}_j}$. One can say that the internal Hamiltonian, (3), is a generalized atomic Hamiltonian due to its spherical symmetry. However, while in an atom the moving particles are all electrons with minus one (in a.u.) charges, in the generalized atom represented by (3) the moving pseudoparticles can have negative (-1) and positive charges. As the internal Hamiltonian is fully symmetric (isotropic) with respect to all rotations around the center of the internal coordinate system, its wave functions transform as irreducible representations of the fully symmetric group of rotations (like for atoms).

III. CORRELATED GAUSSIAN BASIS SET

The generalized atomic Hamiltonian commutes with the the square of the total angular momentum operator. Thus, if one uses basis functions which are eigenfunctions of that operator in expanding the wave functions of the molecular system under consideration, states corresponding to different total-angular-momentum quantum numbers are separated. In particular, if one considers only the rotationless states (i.e., states with the zero total angular momentum or pure vibrational states), as we do in the present work, one needs to use fully spherically symmetric basis functions. When ECGs are used as such functions for an atomic system with s electrons, they have the following form:

$$\psi_k(\mathbf{r}) = \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}], \quad (5)$$

where $\bar{\mathbf{A}}_k$ is a symmetric matrix of the variational exponential parameters and T denotes the transpose. $\bar{\mathbf{A}}_k$ can be written as $\bar{\mathbf{A}}_k = \mathbf{A}_k \otimes \mathbf{I}_3$, where $\mathbf{I}_3$ is the 3×3 unit matrix. To ensure square integrability of $\psi_k(\mathbf{r})$, $\mathbf{A}_k$ has to be positive definite. To ensure that, $\mathbf{A}_k$ is represented in the Cholesky factored form as $\mathbf{A}_k = \mathbf{L}_k \mathbf{L}_k^T$, where $\mathbf{L}_k$ is an $n \times n$, rank n, lower triangular matrix. $\psi_k(\mathbf{r})$ is square-integrable for $\mathbf{L}_k$ matrix elements being any real numbers. Function (5) is invariant upon any orthogonal unitary transformation representing a rotation about the center of the internal coordinate frame.

Let us now consider a diatomic system, for example, the HD$^+$ ion, in rotationless states. The ECGs for such states have to also be spherically symmetric, but the non-BO wave functions now have to describe the correlated motion of two pseudoparticles, one of which has a charge of -1 (pseudoelectron), but the other one has a positive charge (pseudonucleus). As the pseudonucleus is repelled by the central positive charge of the reference nucleus (the deuteron for HD$^+$), the ECGs have to describe a deep "Coulomb hole" in the wave function resulting from this repulsion. Also, if excited vibrational states are considered in the calculations, whose wave functions have nodes in terms of the internuclear distance coordinate (this coordinate is r_1 in the internal coordinate frame), the atomic ECGs (5) need to be multiplied

by nonnegative powers of this coordinate:

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}^T(\mathbf{A}_k \otimes I_3)\mathbf{r}] = r_1^{m_k} \exp[-\mathbf{r}^T \bar{\mathbf{A}}_k \mathbf{r}], \quad (6)$$

where $r_1 = |\mathbf{R}_2 - \mathbf{R}_1|$. The factor $r_1^{m_k}$ shifts the maximum of the Gaussian away from the reference particle (which is located in the center of the coordinate system) to a sphere with a radius, which depends on the m_k power. The higher is the power the larger is the radius. In our calculations the m_k powers range from 0 to 250 and they are either zero or even numbers. These powers are variational parameters which are optimized in the calculation along with the matrix elements of $\mathbf{L}_k$.

The use of only even powers of the internuclear distance as preexponential multipliers of the Gaussians would be a problem, if the probability of two nuclei being in a single point in space were not negligible and the cusp behavior had to be accurately described. But this probability is negligible and the description of the internuclear cusp has no effect on the energy. As the use of the even powers considerably simplifies the calculation, only such powers are used here. There is, however, another reason why functions (6) may not be as effective as Hylleraas-type or Slater-type basis functions. This has to do with the correct description of the behavior of the electrons (the electron in the case of HD$^+$) when they approach the nuclei and when they approach each other. The use of Gaussians, due to their improper representation of the electron-nucleus and electron-electron cusps, may lead to longer expansions of the wave function to achieve adequate accuracy in the calculations.

To obtain the energy eigenvalues of Hamiltonian (3) the Rayleigh-Ritz variational scheme based on the minimization of the Rayleigh quotient,

$$\varepsilon(\mathsf{a},\mathsf{c}) = \min_{(\mathsf{a},\mathsf{c})} \frac{\mathsf{c}^T \mathsf{H}(\mathsf{a})\mathsf{c}}{\mathsf{c}^T \mathsf{S}(\mathsf{a})\mathsf{c}}, \quad (7)$$

is used, where $\mathsf{H}(\mathsf{a})$ and $\mathsf{S}(\mathsf{a})$ are the Hamiltonian and overlap matrices, respectively. Equation (7) is minimized in terms of the $\mathbf{L}_k$ parameters and m_k powers represented in (7) by (a), and the linear expansion coefficients (c) of the wave function in terms of ECGs. To accelerate the minimization of (7) with respect to $\mathbf{L}_k$, which is the most time-consuming step of the calculation, we use the analytic energy gradient determined with respect to the $\mathbf{L}_k$ matrix elements [9].

A. Relativistic operators

The Breit-Pauli relativistic Hamiltonian [17], H^{rel}, is used in this work to calculate the leading relativistic corrections. As the wave function generated in our non-BO calculation describes the motion of pseudoparticles in the internal coordinate system, there are two ways the calculations of the relativistic corrections can be carried out. The first way is to back-transform the pseudoparticle wave function to describe the real particles and then use this back-transformed wave function and the Breit-Pauli Hamiltonian in its original form expressed in the laboratory coordinates to calculate the relativistic corrections. An analysis of Korobov's work [18,19] shows that this seems to be the approach he takes. The second way, which is employed here, involves transforming the laboratory-frame Breit-Pauli Hamiltonian to the coordinate system used in the present calculations and use this transformed Hamiltonian and the non-BO pseudoparticle wave functions to determine the

relativistic corrections. The transformation of the Breit-Pauli from the laboratory coordinates to the internal coordinates was shown before [7,13]. After the transformation the Breit-Pauli Hamiltonian becomes a function of the coordinates of the center of mass, $\mathbf{r}_0$, and the internal coordinates, $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$, and splits into three contributions:

$$H^{\mathrm{rel}}(\mathbf{r},\mathbf{r}_0) = H^{\mathrm{rel}}_{\mathrm{cm}}(\mathbf{r}_0) + H^{\mathrm{rel}}_{\mathrm{int}}(\mathbf{r}) + H^{\mathrm{rel}}_{\mathrm{cm-int}}(\mathbf{r},\mathbf{r}_0), \quad (8)$$

where $H^{\mathrm{rel}}_{\mathrm{cm}}(\mathbf{r}_0)$ is the term describing the relativistic effects associated with the motion of the center of mass, $H^{\mathrm{rel}}_{\mathrm{int}}(\mathbf{r})$ describes the internal relativistic effects, and $H^{\mathrm{rel}}_{\mathrm{cm-int}}(\mathbf{r},\mathbf{r}_0)$ describes the relativistic coupling of the internal and external motions. The appearance of this last term results from using in the transformation a coordinate system, which allows for a rigorous separation of the external motion (the motion of the center of mass) from the internal motion in the nonrelativistic Hamiltonian, but does not allow for separation of the relativistic effects in the same manner. This lack of full separability has its origin in the coordinate system used in the transformation involving the center of mass and not the center of the total linear momentum. In general, the center of mass in the relativistic quantum mechanics is not unambiguously defined because the masses of the particles depend on their velocities. In the nonrelativistic approach the center of mass and the center of the total linear momentum are identical and the separation of the total nonrelativistic laboratory-frame Hamiltonian into the internal Hamiltonian and the Hamiltonian representing the center-of-mass motion can be rigorously achieved.

The coupling term in the Breit-Pauli relativistic Hamiltonian, $H^{\mathrm{rel}}_{\mathrm{cm-int}}(\mathbf{r},\mathbf{r}_0)$, resulting from the coordinate transformation can be symbolically written as $P_0 W(R) + P_0^2 Q(R)$, where P_0 is the momentum of the center-of-mass motion, and $W(R)$ and $Q(R)$ are operators which do not depend on the center-of-mass coordinates. Let us now take a total wave function for the system in the form of a product of the wave function describing the state of the center of mass and dependent only on $\mathbf{r}_0$, and an $\mathbf{r}_0$-independent wave function describing the internal state of the system (such a product wave function is the correct form of the nonrelativistic wave function). If such a function is used to calculate the expectation value of the coupling term, $H^{\mathrm{rel}}_{\mathrm{cm-int}}(\mathbf{r},\mathbf{r}_0)$, a product of the average value of the linear momentum of the center-of-mass and matrix elements of the W or Q operators is obtained. If one assumes that the center-of-mass momentum is zero, the contribution of the coupling term to the relativistic correction vanishes. Thus, in this limit the approach used in the present calculations of the relativistic correction is correct. However, a slight difference may still appear between the present results and the results obtained with the approach based on the BO approximation. That difference includes the so-called recoil correction, but it may also include relativistic effects due to the internal motion of the nuclei.

Thus $H^{\mathrm{rel}}_{\mathrm{int}}(\mathbf{r})$ is used in the present calculations to determine the relativistic correction. The explicit form of the components of $H^{\mathrm{rel}}_{\mathrm{int}}(\mathbf{r})$ accounting for the mass-velocity (MV), Darwin (D), and orbit-orbit (OO) interactions in HD$^+$ are as

follows [7,13]:

$$\hat{H}_{MV}(\mathbf{r}) = -\frac{1}{8}\left[\frac{1}{m_0^3}\left(\sum_{i=1}^2 \boldsymbol{\nabla}_{\mathbf{r}_i}\right)^4 + \sum_{i=1}^2 \frac{1}{m_i^3}\nabla_{\mathbf{r}_i}^4\right], \quad (9)$$

$$\hat{H}_D(\mathbf{r}) = \frac{\pi}{2}\sum_{i=1}^2\left(\frac{4}{3}\frac{1}{m_0^2} + \frac{1}{m_i^2}\right)q_0 q_i\, \delta^3(r_i)$$

$$+ \frac{\pi}{2}\sum_{i=1}^2\sum_{j\neq i}^2 \frac{1}{m_i^2}q_i q_j\, \delta^3(r_{ij}), \quad (10)$$

$$\hat{H}_{OO}(\mathbf{r}) = -\frac{1}{2}\sum_{i=1}^2\sum_{j=1}^2 \frac{q_0 q_j}{m_0 m_j}$$

$$\times\left[\frac{1}{r_j}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_j^3}\mathbf{r}_j\cdot(\mathbf{r}_j\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right]$$

$$+ \frac{1}{2}\sum_{i=1}^2\sum_{j>i}^2 \frac{q_i q_j}{m_i m_j}$$

$$\times\left[\frac{1}{r_{ij}}\boldsymbol{\nabla}_{\mathbf{r}_i}\cdot\boldsymbol{\nabla}_{\mathbf{r}_j} + \frac{1}{r_{ij}^3}\mathbf{r}_{ij}\cdot(\mathbf{r}_{ij}\cdot\boldsymbol{\nabla}_{\mathbf{r}_i})\boldsymbol{\nabla}_{\mathbf{r}_j}\right].$$

$$(11)$$

As was the case in the work of Korobov [18,19] the spin-spin hyperfine interactions are not included in the present calculations. Thus, the transition energies do not include the hyperfine splittings of the lines which originate from these interactions. Also, as the considered states of HD$^+$ have zero total angular momentum, the spin-orbit interaction is zero.

IV. NUMERICAL RESULTS

As mentioned, the non-BO nonrelativistic calculations are done using the standard variational method. Each state is calculated separately from other states. In the calculation a ECG basis set for each state is generated and optimized.

We will now describe the results of the calculations of the pure vibrational spectrum of HD$^+$ performed in this work. The first step of the calculations involves doubling (or in some cases tripling) the number of ECGs in the basis set for each state from the number of ECGs used in our previous calculations [7]. Adding new Gaussians to the basis set is done incrementally. The functions are added in the subsets of 100, one function at time. The initial values of the $\mathbf{L}_k$ parameters for a newly added function are obtained by adding random perturbations to one of the most contributing functions already included in the basis set. The new function, before it is optimized with the gradient-based optimization procedure, is check for linear dependency with the functions already included in the set. If

TABLE I. The convergence of the total nonrelativistic non-BO energies of the pure vibrational states of HD$^+$. All values are given in a.u. (hartrees).

v	No. ECGs	Energy	v	No. ECGs	Energy	v	No. ECGs	Energy	v	No. ECGs	Energy
0	2000	$-0.597\,897\,968\,460$	1	2000	$-0.589\,181\,829\,062$	2	2000	$-0.580\,903\,700\,134$	3	2000	$-0.573\,050\,546\,235$
	3000	$-0.597\,897\,968\,564$		3000	$-0.589\,181\,829\,497$		3000	$-0.580\,903\,700\,198$		3000	$-0.573\,050\,546\,421$
	4000	$-0.597\,897\,968\,577$		4000	$-0.589\,181\,829\,537$		4000	$-0.580\,903\,700\,201$		4000	$-0.573\,050\,546\,451$
4	2000	$-0.565\,611\,041\,772$	5	2000	$-0.558\,575\,519\,997$	6	2000	$-0.551\,935\,947\,607$	7	2000	$-0.545\,685\,913\,715$
	3000	$-0.565\,611\,041\,956$		3000	$-0.558\,575\,520\,589$		3000	$-0.551\,935\,948\,442$		3000	$-0.545\,685\,914\,874$
	4000	$-0.565\,611\,042\,015$		4000	$-0.558\,575\,520\,667$		4000	$-0.551\,935\,948\,624$		4000	$-0.545\,685\,914\,996$
8	2000	$-0.539\,820\,639\,350$	9	2000	$-0.534\,337\,010\,968$	10	2000	$-0.529\,233\,631\,698$	11	2000	$-0.524\,510\,905\,881$
	3000	$-0.539\,820\,640\,428$		3000	$-0.534\,337\,012\,858$		3000	$-0.529\,233\,634\,350$		3000	$-0.524\,510\,909\,188$
	4000	$-0.539\,820\,640\,553$		4000	$-0.534\,337\,013\,108$		4000	$-0.529\,233\,634\,746$		4000	$-0.524\,510\,909\,642$
12	2000	$-0.520\,171\,137\,438$	13	2000	$-0.516\,218\,698\,798$	14	2000	$-0.512\,660\,176\,700$	15	2000	$-0.509\,504\,627\,044$
	3000	$-0.520\,171\,143\,409$		3000	$-0.516\,218\,708\,132$		3000	$-0.512\,660\,189\,014$		3000	$-0.509\,504\,645\,408$
	4000	$-0.520\,171\,143\,836$		4000	$-0.516\,218\,708\,878$		4000	$-0.512\,660\,190\,557$		4000	$-0.509\,504\,646\,834$
							5000	$-0.512\,660\,191\,254$		5000	$-0.509\,504\,647\,412$
16	2000	$-0.506\,763\,834\,484$	17	2000	$-0.504\,452\,646\,624$	18	2000	$-0.502\,589\,181\,516$	19	2000	$-0.501\,194\,732\,351$
	3000	$-0.506\,763\,867\,392$		3000	$-0.504\,452\,682\,298$		3000	$-0.502\,589\,214\,075$		3000	$-0.501\,194\,778\,027$
	4000	$-0.506\,763\,872\,653$		4000	$-0.504\,452\,688\,975$		4000	$-0.502\,589\,222\,933$		4000	$-0.501\,194\,793\,303$
	5000	$-0.506\,763\,873\,462$		5000	$-0.504\,452\,691\,193$		5000	$-0.502\,589\,226\,578$		5000	$-0.501\,194\,792\,626$
	6000	$-0.506\,763\,873\,837$		6000	$-0.504\,452\,691\,747$		6000	$-0.502\,589\,227\,342$		6000	$-0.501\,194\,793\,351$
										7000	$-0.501\,194\,794\,224$
20	2000	$-0.500\,292\,401\,660$	21	2000	$-0.499\,910\,333\,885$	22	4000	$-0.499\,865\,777\,505$			
	3000	$-0.500\,292\,446\,616$		3000	$-0.499\,910\,356\,535$		5000	$-0.499\,865\,778\,116$			
	4000	$-0.500\,292\,451\,530$		4000	$-0.499\,910\,358\,905$		6000	$-0.499\,865\,778\,267$			
	5000	$-0.500\,292\,452\,970$		5000	$-0.499\,910\,359\,126$		7000	$-0.499\,865\,778\,308$			
	6000	$-0.500\,292\,453\,455$		6000	$-0.499\,910\,359\,337$						
	7000	$-0.500\,292\,453\,636$		7000	$-0.499\,910\,359\,483$						

none is found, its m_k power is optimized (this is the only time the power of the ECG is optimized) and then the optimization of its $\mathbf{L}_k$ parameters is carried out. After the optimization the function is again checked for linear dependency and it is included in the basis set only if no linear dependency is found. After each 100-function subset is added to the basis set, the whole basis is reoptimized in a cyclic optimization where each function is separately optimized with the gradient-based method. The cyclic optimization is repeated several times after each addition of 1000 functions. This rather elaborate optimization procedure allows for very tight convergence of the total energy of each state. Also, the increase of the basis set size is carried out for each state to the point when the changes in the total energy are smaller than 10^{-9} hartrees. This means that for lower states smaller numbers of ECGs in the basis sets are generated than for higher states, as the wave functions with fewer number of nodes require less ECGs to be represented.

The convergence of the total energies for all 23 pure vibrational states of HD$^+$ is shown in Table I. As one can see, the target convergence of below 10^{-9} hartrees is reached for all states. The size of the basis set is increased to 4000 for the ground $v = 0$ state and to 7000 for the four top states. It should be mentioned that in the previous calculations of the pure vibrational spectrum of HD$^+$ by Howells and Kennedy [20] the highest 23rd state was not described.

In the non-BO approach used in this work the relativistic corrections to the energies of the pure vibrational states of HD$^+$ are obtained as expectation values of the relativistic operators using the all-particle wave functions obtained in the non-BO calculations. The non-BO approach was also used by Korobov [18,19] and by Zhong *et al.* [21]. However, as mentioned, their relativistic corrections were calculated with a somewhat different procedure than the one used in the present work. Also, due to the use of Slater-type rather than Gaussian-type basis functions by Korobov and Zhong *et al.* their results are likely to be more accurate than ours. However, they only calculated the lowest five vibrational states, while in the present work all 23 bound pure vibrational states of HD$^+$ are considered.

There are two reasons why the present results for the relativistic corrections, as well as the results obtained by Korobov [19] and Zhong *et al.* [21], are not strictly identical to the results obtained in the conventional approach where the BO approximation is assumed. The first one is related to the present relativistic corrections including the contributions due to both nuclei and electrons, while the results of the conventional approach include only the electronic relativistic contribution. The second reason is due to the vibrational wave functions in the conventional approach being dependent on the relativistic effects as they are generated using a potential which includes the electronic relativistic corrections, while the non-BO wave functions obtained in the present approach (a part of the non-BO wave function describes the vibrational state of the molecule) do not include any relativistic effects. These effects are accounted for using the first-order perturbation theory after the non-BO calculations are completed.

The results of the calculations of the relativistic corrections performed in this work are presented in Table II. For each state the convergence of the individual relativistic contributions [i.e.,

TABLE II. Expectation values of the operators representing the leading relativistic corrections: mass-velocity (MV), Darwin (D), orbit-orbit (OO), and the total non-BO relativistic correction ($\alpha^2 E_{\text{rel}}$). All values are given in cm^{-1}.

v	Basis	MV	D	OO	$\alpha^2 E_{\text{rel}}$
0	2000	−9.1989	7.6026	−5.59×10^{-3}	−1.6019
	3000	−9.2005	7.6042	−5.59×10^{-3}	−1.6020
	4000	−9.2010	7.6046	−5.59×10^{-3}	−1.6020
1	2000	−8.9900	7.4257	−5.46×10^{-3}	−1.5698
	3000	−8.9942	7.4297	−5.46×10^{-3}	−1.5700
	4000	−8.9955	7.4309	−5.46×10^{-3}	−1.5701
	5000	−8.9955	7.4309	−5.46×10^{-3}	−1.5700
2	2000	−8.8012	7.2658	−5.33×10^{-3}	−1.5407
	3000	−8.8033	7.2678	−5.33×10^{-3}	−1.5409
	4000	−8.8036	7.2679	−5.33×10^{-3}	−1.5410
3	2000	−8.6224	7.1131	−5.22×10^{-3}	−1.5145
	3000	−8.6227	7.1135	−5.22×10^{-3}	−1.5145
	4000	−8.6232	7.1139	−5.22×10^{-3}	−1.5145
4	2000	−8.4547	6.9691	−5.12×10^{-3}	−1.4907
	3000	−8.4570	6.9719	−5.12×10^{-3}	−1.4902
	4000	−8.4583	6.9726	−5.12×10^{-3}	−1.4907
5	2000	−8.2995	6.8356	−5.03×10^{-3}	−1.4689
	3000	−8.3033	6.8389	−5.03×10^{-3}	−1.4694
	4000	−8.3043	6.8394	−5.03×10^{-3}	−1.4699
6	2000	−8.1592	6.7138	−4.94×10^{-3}	−1.4504
	3000	−8.1607	6.7152	−4.94×10^{-3}	−1.4505
	4000	−8.1612	6.7157	−4.94×10^{-3}	−1.4505
7	2000	−8.0275	6.5984	−4.87×10^{-3}	−1.4340
	3000	−8.0301	6.6010	−4.87×10^{-3}	−1.4340
	4000	−8.0310	6.6018	−4.87×10^{-3}	−1.4340
8	2000	−7.9069	6.4919	−4.80×10^{-3}	−1.4198
	3000	−7.9099	6.4947	−4.80×10^{-3}	−1.4200
	4000	−7.9099	6.4948	−4.80×10^{-3}	−1.4199
9	2000	−7.7995	6.3962	−4.74×10^{-3}	−1.4080
	3000	−7.8018	6.3984	−4.74×10^{-3}	−1.4081
	4000	−7.8023	6.3989	−4.74×10^{-3}	−1.4081
10	2000	−7.6988	6.3050	−4.69×10^{-3}	−1.3986
	3000	−7.7013	6.3075	−4.69×10^{-3}	−1.3985
	4000	−7.7018	6.3079	−4.69×10^{-3}	−1.3985
11	2000	−7.6118	6.2251	−4.65×10^{-3}	−1.3914
	3000	−7.6151	6.2283	−4.65×10^{-3}	−1.3914
	4000	−7.6155	6.2287	−4.65×10^{-3}	−1.3914
12	2000	−7.5258	6.1436	−4.61×10^{-3}	−1.3869
	3000	−7.5290	6.1474	−4.61×10^{-3}	−1.3863
	4000	−7.5292	6.1475	−4.61×10^{-3}	−1.3863
13	2000	−7.4618	6.0825	−4.59×10^{-3}	−1.3839
	3000	−7.4663	6.0869	−4.59×10^{-3}	−1.3840
	4000	−7.4673	6.0878	−4.59×10^{-3}	−1.3841
14	2000	−7.4005	6.0213	−4.57×10^{-3}	−1.3838
	3000	−7.4055	6.0262	−4.57×10^{-3}	−1.3839
	4000	−7.4060	6.0267	−4.57×10^{-3}	−1.3838
	5000	−7.4072	6.0279	−4.57×10^{-3}	−1.3839
15	2000	−7.3498	5.9681	−4.57×10^{-3}	−1.3863
	3000	−7.3565	5.9745	−4.57×10^{-3}	−1.3866
	4000	−7.3567	5.9748	−4.57×10^{-3}	−1.3865
	5000	−7.3569	5.9749	−4.57×10^{-3}	−1.3865
16	2000	−7.3079	5.9213	−4.57×10^{-3}	−1.3911
	3000	−7.3106	5.9242	−4.57×10^{-3}	−1.3909
	4000	−7.3155	5.9290	−4.57×10^{-3}	−1.3911
	5000	−7.3160	5.9295	−4.57×10^{-3}	−1.3911

TABLE II. (*Continued.*)

v	Basis	MV	D	OO	$\alpha^2 E_{\text{rel}}$
	6000	−7.3161	5.9295	-4.57×10^{-3}	−1.3911
17	2000	−7.2749	5.8810	-4.58×10^{-3}	−1.3984
	3000	−7.2804	5.8864	-4.58×10^{-3}	−1.3986
	4000	−7.2837	5.8898	-4.58×10^{-3}	−1.3984
	5000	−7.2867	5.8926	-4.58×10^{-3}	−1.3987
	6000	−7.2867	5.8926	-4.58×10^{-3}	−1.3987
18	2000	−7.2556	5.8513	-4.59×10^{-3}	−1.4088
	3000	−7.2599	5.8559	-4.59×10^{-3}	−1.4086
	4000	−7.2627	5.8588	-4.59×10^{-3}	−1.4085
	5000	−7.2672	5.8629	-4.59×10^{-3}	−1.4088
	6000	−7.2675	5.8632	-4.59×10^{-3}	−1.4089
19	2000	−7.2488	5.8318	-4.60×10^{-3}	−1.4216
	3000	−7.2516	5.8348	-4.60×10^{-3}	−1.4214
	4000	−7.2588	5.8417	-4.60×10^{-3}	−1.4217
	5000	−7.2593	5.8421	-4.60×10^{-3}	−1.4218
	6000	−7.2595	5.8422	-4.60×10^{-3}	−1.4219
	7000	−7.2609	5.8435	-4.60×10^{-3}	−1.4220
20	2000	−7.2589	5.8259	-4.52×10^{-3}	−1.4375
	3000	−7.2645	5.8314	-4.52×10^{-3}	−1.4377
	4000	−7.2653	5.8323	-4.52×10^{-3}	−1.4375
	5000	−7.2669	5.8338	-4.52×10^{-3}	−1.4376
	6000	−7.2675	5.8344	-4.52×10^{-3}	−1.4376
	7000	−7.2676	5.8345	-4.52×10^{-3}	−1.4376
21	2000	−7.2773	5.8248	-3.48×10^{-3}	−1.4559
	3000	−7.2867	5.8339	-3.48×10^{-3}	−1.4563
	4000	−7.2869	5.8341	-3.48×10^{-3}	−1.4563
	5000	−7.2871	5.8343	-3.48×10^{-3}	−1.4563
	6000	−7.2872	5.8343	-3.48×10^{-3}	−1.4563
	7000	−7.2872	5.8344	-3.48×10^{-3}	−1.4564
22	4000	−7.2947	5.8375	-3.22×10^{-3}	−1.4604
	5000	−7.2949	5.8377	-3.22×10^{-3}	−1.4604
	6000	−7.2953	5.8381	-3.22×10^{-3}	−1.4604
	7000	−7.2953	5.8381	-3.22×10^{-3}	−1.4604
	$\text{D}+\text{H}^+$	−7.2966	5.8389	-3.18×10^{-3}	−1.4609
	D^++H	−7.2887	5.8341	-6.35×10^{-3}	−1.4609

mass-velocity, Darwin (one and two particles), spin-spin, and orbit-orbit], as well as the convergence of the total relativistic correction, is shown. As one can see, the total corrections for all states is convergent to the last-shown fourth digit after the decimal point (in cm^{-1}) with the number of ECGs used for each state.

It is interesting to again (this was also done in our previous work [8]) examine, based on the present more accurate results, how the charge asymmetry, which strongly increases in the top vibrational states of HD$^+$, affects the values of the total relativistic correction and the individual relativistic contributions. Assessing this effect can be done by comparing the values with the results for the products of the two possible dissociation paths, i.e., the lowest-energy dissociation path which yields a deuterium and a proton and the dissociation path which yields products with a slightly higher energy, i.e., a deuteron and a hydrogen atom (see the last two lines in Table II). As one can see, the mass-velocity, Darwin, and orbit-orbit relativistic corrections converge, as expected, to the $\text{D}+\text{H}^+$ results. This adds credibility to the way these

TABLE III. Convergence of the total energy, which includes the the nonrelativistic energy (E_{nr}) and the α^2 correction ($\alpha^2 E_{\text{rel}}$), in a.u. (hartrees) and the HD$^+$ dissociation energy for the different vibrational states in cm^{-1}. Factor 219 474.631 370 8(11) cm^{-1}/hartree is used to convert the results in hartrees to cm^{-1}.

v	Basis	$E_{\text{nr}}+\alpha^2 E_{\text{rel}}$	$E(\text{H}^++\text{D})-E(\text{HD}^+)$
0	2000	−0.597 905 267 343	21 516.1507
	3000	−0.597 905 267 667	21 516.1507
	4000	−0.597 905 267 814	21 516.1508
1	2000	−0.589 188 981 611	19 603.1471
	3000	−0.589 188 982 927	19 603.1473
	4000	−0.589 188 983 354	19 603.1474
	5000	−0.589 188 983 189	19 603.1474
2	2000	−0.580 910 720 066	17 786.2787
	3000	−0.580 910 721 065	17 786.2789
	4000	−0.580 910 721 736	17 786.2790
3	2000	−0.573 057 446 617	16 062.6844
	3000	−0.573 057 446 799	16 062.6844
	4000	−0.573 057 446 928	16 062.6844
4	2000	−0.565 617 833 831	14 429.8781
	3000	−0.565 617 831 941	14 429.8777
	4000	−0.565 617 834 361	14 429.8782
5	2000	−0.558 582 213 014	12 885.7378
	3000	−0.558 582 215 774	12 885.7384
	4000	−0.558 582 217 931	12 885.7389
6	2000	−0.551 942 556 150	11 428.5016
	3000	−0.551 942 557 255	11 428.5018
	4000	−0.551 942 557 517	11 428.5019
7	2000	−0.545 692 447 411	10 056.7612
	3000	−0.545 692 448 469	10 056.7615
	4000	−0.545 692 448 763	10 056.7615
8	2000	−0.539 827 108 217	8 769.4681
	3000	−0.539 827 110 211	8 769.4685
	4000	−0.539 827 110 296	8 769.4685
9	2000	−0.534 343 426 432	7 565.9390
	3000	−0.534 343 428 597	7 565.9395
	4000	−0.534 343 428 972	7 565.9396
10	2000	−0.529 240 004 058	6 445.8673
	3000	−0.529 240 006 508	6 445.8678
	4000	−0.529 240 006 914	6 445.8679
11	2000	−0.524 517 245 411	5 409.3416
	3000	−0.524 517 249 004	5 409.3424
	4000	−0.524 517 249 547	5 409.3425
12	2000	−0.520 177 456 502	4 456.8680
	3000	−0.520 177 459 656	4 456.8687
	4000	−0.520 177 460 305	4 456.8689
13	2000	−0.516 225 004 263	3 589.4050
	3000	−0.516 225 014 206	3 589.4072
	4000	−0.516 225 015 297	3 589.4074
14	2000	−0.512 666 482 163	2 808.3997
	3000	−0.512 666 494 478	2 808.4024
	4000	−0.512 666 495 818	2 808.4027
	5000	−0.512 666 496 717	2 808.4029
15	2000	−0.509 510 943 549	2 115.8390
	3000	−0.509 510 963 295	2 115.8434
	4000	−0.509 510 964 292	2 115.8436
	5000	−0.509 510 964 875	2 115.8437
16	2000	−0.506 770 172 715	1 514.3094
	3000	−0.506 770 204 853	1 514.3164
	4000	−0.506 770 210 795	1 514.3177

TABLE III. (*Continued.*)

v	Basis	$E_{nr} + \alpha^2 E_{rel}$	$E(H^+ + D) - E(HD^+)$
	5000	−0.506 770 211 813	1 514.3179
	6000	−0.506 770 212 303	1 514.3180
17	2000	−0.504 459 018 320	1 007.0696
	3000	−0.504 459 054 629	1 007.0776
	4000	−0.504 459 060 682	1 007.0789
	5000	−0.504 459 064 188	1 007.0797
	6000	−0.504 459 064 592	1 007.0798
18	2000	−0.502 595 600 480	598.0967
	3000	−0.502 595 632 079	598.1036
	4000	−0.502 595 640 731	598.1055
	5000	−0.502 595 645 753	598.1066
	6000	−0.502 595 646 667	598.1068
19	2000	−0.501 201 209 459	292.0632
	3000	−0.501 201 254 421	292.0731
	4000	−0.501 201 271 189	292.0767
	5000	−0.501 201 270 867	292.0767
	6000	−0.501 201 271 858	292.0769
	7000	−0.501 201 273 411	292.0772
20	2000	−0.500 298 951 269	94.0404
	3000	−0.500 298 997 194	94.0505
	4000	−0.500 299 001 358	94.0514
	5000	−0.500 299 003 295	94.0518
	6000	−0.500 299 003 773	94.0519
	7000	−0.500 299 003 850	94.0520
21	2000	−0.499 916 967 542	10.2047
	3000	−0.499 916 992 065	10.2101
	4000	−0.499 916 994 072	10.2105
	5000	−0.499 916 994 609	10.2106
	6000	−0.499 916 994 955	10.2107
	7000	−0.499 916 995 200	10.2107
22	4000	−0.499 872 431 585	0.4302
	5000	−0.499 872 432 210	0.4303
	6000	−0.499 872 432 563	0.4304
	7000	−0.499 872 432 478	0.4304
D + H$^+$		−0.499 870 471 620	

corrections are calculated in the present work. The D + H$^+$ results are noticeably different from the D$^+$ + H results. Also, the total relativistic correction converges to the D + H$^+$ result. However this result is identical to the D$^+$ + H result as the recoil correction for an one-electron atom vanishes.

In Table III we show the total energy obtained as a sum of the nonrelativistic energy plus the leading relativistic correction for each state and the corresponding dissociation energy calculated with respect to the D + H$^+$ dissociation limit. This latter value should be considered converged to about 0.0001–0.0003 cm^{-1}.

Finally, in Table IV we show a comparison of the contributions from the nonrelativistic energy and from the relativistic correction to the $v = 0 \rightarrow v = 1$ transition energy (in MHz) obtained in the present calculations with the corresponding values taken from the very accurate calculations of Korobov [18,19]. As one can see, the nonrelativistic energies are virtually identical, while there is a difference of about 6 MHz in the relativistic correction. As mentioned, this difference is likely due to the different algorithms for calculating the

TABLE IV. The $v = 0 \rightarrow v = 1$ transition energy (in MHz) which includes the nonrelativistic and relativistic contributions in comparison with the values obtained by Korobov [18,19]. The relativistic contribution does not include the spin-spin interaction. CODATA12 [22] recommended values have been used in the present calculations. The result marked with * is obtained using the values calculated with 5000 ECGs for the $v = 1$ state and 4000 ECGs for the $v = 0$ state. Factor 6 579 683 920.729(33) MHz/hartree is used to convert the results expressed in hartrees to MHz.

No. ECGs	Present Work	Ref. [19]
E_{nr}		
2000	57 349 442.2539	
3000	57 349 440.0693	
4000	57 349 439.8957	57 349 439.9717
5000*	57 349 439.8635	
$\alpha^2 E_{rel}$		
2000	962.828	
3000	958.480	
4000	956.817	958.152
5000*	957.933	

corrections and due to the different types of the basis functions used. As the expectation values of the relativistic operators are sensitive to the cusp behavior of the wave function, they are calculated more accurately using Slater-type functions, such as the ones employed by Korobov [19] and Zhong *et al.* [21], than with the Gaussian-type functions. Thus the comparison with Korobov's results provides a good test of the accuracy of the relativistic corrections calculated in this work.

V. SUMMARY

High-quality non-BO calculations are performed for all pure vibrational states of the HD$^+$ ion with explicitly correlated Gaussian functions multiplied by even powers of the internuclear distance. The analytic energy gradient determined with respect to the Gaussian exponential parameters is used in the variational optimization of these parameters. The non-BO wave functions of the states are expanded in terms of 4000 to 7000 Gaussians. Subsequently these wave functions are used to calculate the leading relativistic corrections using the first-order perturbation theory. It is shown that the individual contributions to the relativistic correction converge to the values obtained for the D + H$^+$ dissociation products as the level of the vibrational excitation increases. The total energies of the considered states obtained by summing the nonrelativistic energies and the relativistic corrections are used to determine the corresponding dissociation energies.

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