

Charge asymmetry in HD^+

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Expanding the wave functions of the ground and excited states of HD^+ (or *pde*) in terms of spherically symmetric explicitly correlated Gaussian functions with preexponential multipliers consisting of powers of the internuclear distance, and using the variational method, we performed very accurate nonadiabatic calculations of all bound states of this system corresponding to the zero total angular momentum quantum number (vibrational states; $v=0-22$). The total and the transition energies obtained agree with the best available calculations. For each state we computed the expectation values of the *d-p*, *d-e*, and *p-e* interparticle distances. This is the first time these quantities were computed for HD^+ using rigorous nonadiabatic wave functions. While up to the $v=20$ state some asymmetry is showing in the *d-e* and *p-e* distances, for $v=21$ and $v=22$ we observe a complete breakdown of the Born–Oppenheimer approximation and localization of the electron almost entirely at the deuteron. © 2005 American Institute of Physics.

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The singly deuterated isotopomer of the H_2 cation, HD^+ , has been used for several decades in model studies of the coupling between the electronic and nuclear motions.¹ In HD^+ the lack of a center of symmetry, due to the different nuclear masses, creates a particularly interesting situation that requires a theoretical approach that may differ from those used to describe the parent cation, H_2^+ , and its symmetric isotopomer, D_2^+ . The asymmetry of the HD^+ system has been investigated both experimentally^{2,3} and theoretically.⁴⁻⁶ In recent work Ben-Itzhak *et al.*² studied the dissociation of the electronic ground state of HD^+ following ionization of HD by fast proton impact and found the $\text{H}^+ + \text{D}(1s)$ dissociation channel is more likely than the $\text{H}(1s) + \text{D}^+$ dissociation channel by about 7%. They attributed this asymmetry breakdown to the finite nuclear mass correction to the Born–Oppenheimer (BO) approximation, which makes the $1s\sigma$ state 3.7 meV lower than the $2p\sigma$ state at the dissociation limit.

Near the dissociation limit the density of states in the HD^+ spectrum increases. If one considers only the ground rotational state manifold (i.e., consider only states with total angular momentum equal to zero), one finds states where the dissociation energy of the system becomes close to the difference between the total energies of the H and D atoms (equal to 29.84 cm^{-1}). The D atom is energetically more stable because it has slightly larger reduced mass than H, which makes the electron slightly closer, on average, approach the nucleus resulting in stronger coulombic attraction and a lower energy. In that region the vibrational wave function that corresponds to, say, $v=20$ combined with the

ground state electronic wave function that places the electron at the proton, has similar energy as the wave function with the vibrational component corresponding to $v=21$ and with the electronic component localizing the electron at the deuteron. Since such two wave functions have the same symmetry, their mixing can occur. This nonadiabatic coupling must be included in the calculation of the dissociation of HD^+ that yields a proton plus a deuterium which is the lowest-energy dissociation product of this system.

In nearly all theoretical treatments of H_2^+ and its isotopes reported in the literature, a body-fixed coordinate system with the origin at the geometric center of the nuclei has been used. For example, in the recent work of Esry and Sadeghpour,⁵ as well as other works,⁷⁻¹⁰ the starting point was the H_2^+ BO Hamiltonian in prolate spheroidal coordinates (PSC); and electronic wave functions and energies were first obtained as a function of the internuclear distance. Since, by definition, the BO Hamiltonian and the electronic BO wave function cannot discriminate between the two dissociation limits, $\text{H}^+ + \text{D}$ and $\text{D}^+ + \text{H}$, the symmetry-breaking term beyond the BO approximation had to be added as a perturbation to account for the isotopically induced HD^+ charge asymmetry. Bishop and Cheung¹¹ applied an alternative approach to HD^+ that did not involve the adiabatic approximation and was based on the variational principle. Also, an approach based on a unitary transformation has been used^{4,12-16} to move the symmetry-breaking term from the kinetic-energy operator to the potential-energy operator as reduced-mass dependent effective charges on the nuclei.

In the approach we use,¹⁷ we begin with the total non-

relativistic Hamiltonian for a molecular system in the laboratory Cartesian coordinate system. All particles present in the system are included in the Hamiltonian. The total number of particles (i.e., the electrons and the nuclei) is set to be $n + 1$ and their masses, charges and positions are denoted as M_i , Q_i , and \mathbf{R}_i , respectively, where $i = 1, \dots, n + 1$. The laboratory frame nonrelativistic Hamiltonian that includes the kinetic energy operator for each particle and Coulombic interactions between each pair of the particles has the following form:

$$\hat{H}_{\text{TOT}} = - \sum_{i=1}^{n+1} \frac{1}{2M_i} \nabla_i^2 + \sum_{i=1}^{n+1} \sum_{j>i}^{n+1} \frac{Q_i Q_j}{R_{ij}}, \quad (1)$$

where $R_{ij} = |\mathbf{R}_j - \mathbf{R}_i|$ are interparticle distances. We then make a transformation to separate the center-of-mass Hamiltonian from the rest, thereby reducing the $n + 1$ -particle problem to an n -pseudoparticle problem described by the internal Hamiltonian, \hat{H} . In this transformation we place a heavy particle (particle 1 with mass M_1 called the reference particle; in the HD^+ calculations that particle was the deuteron) at the center of the internal coordinate system and we refer the other particles to that center particle using the cartesian position vectors \mathbf{r}_i defined as $\mathbf{r}_i = \mathbf{R}_{i+1} - \mathbf{R}_1$. The resulting internal Hamiltonian is

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

where $'$ denotes vector transposition. This Hamiltonian describes a system containing the reference particle in the origin of the coordinates with charge $q_0 = Q_1$ and n pseudoparticles, or internal particles, which are characterized by the reduced masses $m_i = M_1 M_{i+1} / (M_1 + M_{i+1})$ and charges $q_i = Q_{i+1}$. The pseudoparticles are moving in the spherically symmetric potential generated by the reference particle placed at the center of the internal coordinate system. The second term in the parentheses is the mass polarization term, which arises from the transformation of the lab-frame coordinate system to the internal coordinate system and which couples the motion of all the particles. In the potential energy terms r_i and r_{ij} are defined as: $r_i = |\mathbf{r}_i|$ and $r_{ij} = |\mathbf{R}_{j+1} - \mathbf{R}_{i+1}| = |\mathbf{r}_j - \mathbf{r}_i|$.

The present HD^+ calculations involved two pseudoparticles (i.e., pseudoelectron and pseudoproton). Unlike other approaches, no charge-symmetry (gerade or ungerade) was imposed on the basis functions and the charge-asymmetry, if appeared in the wave function, was a direct result of the variational calculation.

We have shown that the explicitly correlated Gaussian basis set involving functions with preexponential multipliers consisting of the internuclear distance, \mathbf{r}_1 , raised to a non-negative power, m_k :^{18–20}

$$\phi_k = r_1^{m_k} \exp[-\mathbf{r}'(A_k \otimes I_3)\mathbf{r}] \quad (3)$$

is capable of very effectively describing nonadiabatic zero-angular-momentum states of diatomic systems with σ elec-

trons. The above function is a one-center correlated Gaussian with exponential coefficients forming the symmetric matrix A_k . \mathbf{r} is a $3n \times 1$ vector of the internal cartesian coordinates, \mathbf{r}_i , of the n pseudoparticles, and I_3 is the 3×3 identity matrix. ϕ_k are rotationally invariant functions as required by the symmetry of the internal ground state problem described by the Hamiltonian (2). The presence of $r_1^{m_k}$ in (3) makes the function peak at some distance away from the origin. This distance depends on the value of m_k and on the exponential parameters, A_k . To describe a diatomic system, the maximum of ϕ_k in terms of r_1 should be around the equilibrium internuclear distance of the system. In the variational calculation the maximum of ϕ_k 's is adjusted by optimization of m_k 's and A_k 's.

The ground and excited-state nonadiabatic wave functions for HD^+ in the present calculations were obtained by directly minimizing the Rayleigh quotient,

$$E(\{c_k\}, \{m_k\}, \{A_k\}) = \min_{\{c_k\}, \{m_k\}, \{A_k\}} \frac{c' H(\{m_k\}, \{A_k\}) c}{c' S(\{m_k\}, \{A_k\}) c}, \quad (4)$$

with respect to the expansion coefficients of the wave function in terms of the basis functions, c_k , the basis-function exponential parameters, $\{A_k\}$, and the preexponential powers, $\{m_k\}$.

To achieve the best results in the parameter optimization with the least computational effort, we have recently implemented a hybrid method that combines the gradient-based optimization with the stochastic selection method.^{21,22} The strategy is based on alternating the gradient-based and the stochastic-based optimizations in growing the basis set from a small initial set generated in a gradient-based optimization to the final set. The basis set for each vibrational state was generated in a separate calculation. To achieve a similar level of accuracy as obtained in the best previous calculations⁷ we used 2000 basis functions for each state except the ground and first excited state where we limited ourselves to 1000-term expansions, as the energies for those states were essentially converged with this number of functions. Also, in additional calculations for the highest excited state ($v = 22$), where we studied the convergence of our approach, we used expansions with up to 4000 basis functions. The range of the preexponential powers, $\{m_k\}$, used was from 0 to 250. The calculations have been carried out at the University of Arizona Center of Computing and Information Technology with the use of an HP Alpha GS1280 supercomputer.

After the wave functions for all 23 ($v = 0, \dots, 22$) states were generated, we calculated the expectation values of the internuclear d - p distance, $\langle r_1 \rangle$, the deuteron–electron (d - e) distance, $\langle r_2 \rangle$, and the proton–electron (p - e) distance, $\langle r_{12} \rangle$, for each state, as well as their squares. The algorithm for calculating the expectation values of nucleus–electron distances was developed and implemented in the present work. It will be described in a separate paper.²³ In the calculations we used the following values for the nuclear masses: $m_d = 3670.482\,965\,2 m_e$, $m_p = 1836.152\,672\,61 m_e$ taken from Ref. 24. Here, m_e stands for the mass of the electron.

TABLE I. Total energies, expectation values of the deuteron–proton distance, r_{d-p} , the deuteron–electron distance, r_{d-e} , and the proton–electron distance, r_{p-e} , and their squares for the vibrational levels of HD⁺ at the rotational ground state. All quantities in atomic units.

v	E , this work	E , Ref. 25	$\langle r_{d-p} \rangle$	$\langle r_{d-e} \rangle$	$\langle r_{p-e} \rangle$	$\langle r_{d-p}^2 \rangle$	$\langle r_{d-e}^2 \rangle$	$\langle r_{p-e}^2 \rangle$
0	-0.597 897 968 5	-0.597 897 968 6	2.055	1.688	1.688	4.268	3.534	3.537
1	-0.589 181 829 1	-0.589 181 829 6	2.171	1.750	1.750	4.855	3.839	3.843
2	-0.580 903 700 1	-0.580 903 700 3	2.292	1.813	1.814	5.492	4.169	4.173
3	-0.573 050 546 4	-0.573 050 546 8	2.417	1.880	1.881	6.185	4.526	4.531
4	-0.565 611 041 8	-0.565 611 042 3	2.547	1.948	1.950	6.942	4.915	4.921
5	-0.558 575 520 0	-0.558 575 521 1	2.683	2.020	2.022	7.771	5.339	5.346
6	-0.551 935 948 2	-0.551 935 949 3	2.825	2.095	2.097	8.682	5.804	5.813
7	-0.545 685 913 7	-0.545 685 915 6	2.975	2.175	2.177	9.689	6.318	6.329
8	-0.539 820 639 4	-0.539 820 641 9	3.135	2.259	2.261	10.81	6.888	6.902
9	-0.534 337 011 0	-0.534 337 013 9	3.305	2.348	2.351	12.06	7.527	7.545
10	-0.529 233 631 7	-0.529 233 635 9	3.489	2.445	2.448	13.48	8.250	8.272
11	-0.524 510 905 9	-0.524 510 910 6	3.689	2.549	2.554	15.09	9.074	9.105
12	-0.520 171 137 4	-0.520 171 148 2	3.909	2.664	2.670	16.96	10.03	10.07
13	-0.516 218 698 8	-0.516 218 710 3	4.154	2.791	2.799	19.16	11.15	11.21
14	-0.512 660 176 7	-0.512 660 192 6	4.432	2.934	2.946	21.79	12.49	12.57
15	-0.509 504 627 0	-0.509 504 651 7	4.754	3.099	3.116	25.01	14.13	14.26
16	-0.506 763 834 4	-0.506 763 878 1	5.138	3.292	3.319	29.11	16.20	16.41
17	-0.504 452 646 6	-0.504 452 699 1	5.611	3.527	3.572	34.55	18.92	19.30
18	-0.502 589 181 5	-0.502 589 234 0	6.227	3.821	3.910	42.25	22.66	23.47
19	-0.501 194 732 3	-0.501 194 799 3	7.099	4.198	4.421	54.35	28.13	30.38
20	-0.500 292 401 7	-0.500 292 454 3	8.550	4.569	5.516	77.74	35.66	46.64
21	-0.499 910 333 9	-0.499 910 361 5	12.95	2.306	12.19	176.0	12.94	168.2
22	-0.499 865 777 5	-0.499 865 778 5	28.62	1.600	28.55	910.0	4.266	911.4
D atom ^a	-0.499 863 815 2			1.500			3.002	

^aIn the ground state.

The effort in the first series of the calculations has been focused on generating very accurate variational wave functions and energies for the rotationless vibrational states of the HD⁺ ion. As mentioned, this system has been studied by many researchers and very accurate, virtually exact nonrelativistic energies have been published in the literature.^{7,25} This includes the energy for the highest vibrational $v=22$ state, which is only about 0.4309 cm^{-1} below the D+H⁺ dissociation limit. In Table I we compare our variational energies with the values of Hilico *et al.*²⁵ As one can see, the values agree very well. The agreement is consistently very good for all the states calculated. We should mention that the energies in the Hilico *et al.* work²⁵ were obtained with the CODATA 86 mass values while in our calculations we used more recent CODATA 2002 masses. However, as we have determined, the effect of the mass difference does not exceed the uncertainty due to the basis incompleteness that we have in our calculations. Our calculations, where we used the old CODATA 86 masses, produced energies shifted down by at most 4×10^{-10} a.u. in comparison to the energies obtained with the CODATA 2002 masses. The highest shift was obtained for states in the middle of the spectrum with v near 10. For the lower and higher states the difference due to the CODATA 86/CODATA 2002 mass change was progressively smaller.

In the next step the wave functions for all the 23 states were used to calculate the average internuclear distances and the average distances between the nuclei and the electron. Also, averages of the squares of the distances were calculated. The results are shown in Table I. As can be expected, the average internuclear distance increases with the rising

level of excitation. This increase becomes more prominent at the levels near the dissociation threshold. For example, in going from $v=21$ to $v=22$ the average internuclear distance increases more than twofold from 12.95 a.u. to 28.62 a.u. In the $v=22$ state the HD⁺ ion is almost dissociated. These results agree well with the previous calculations of Moss.²⁶ However, the most striking feature that becomes apparent upon examining the results is a sudden increase of the asymmetry between the deuteron–electron and proton–electron average distances above the $v=20$ excitation level. In levels up to $v=20$ there is some asymmetry of the electron distribution with the $p-e$ distance being slightly longer than the $d-e$ distance. For example, in the $v=20$ state the $d-e$ average distance is 4.569 a.u. and the $p-e$ distance is 5.516 a.u. The situation becomes completely different for the $v=21$ state. Here the $p-e$ distance of 12.19 a.u. is almost equal to the average value of the internuclear distance but the $d-e$ distance becomes much smaller and equals only 2.306 a.u. It is apparent that in this state the electron is essentially localized at the deuteron and the ion becomes highly polarized. An analogous situation also occurs for the $v=22$ state. Here, again, the $p-e$ average distance is very close to the internuclear distance while the $d-e$ distance is close to what it is in an isolated D atom.

To illustrate the convergence of the expectation value calculations, we show in Table II the results for the highest $v=22$ state obtained with different basis sizes. We should note that the $v=22$ state is the most difficult to describe due to its closeness to the dissociation limit and due to the highest number of radial nodes in its wave function. The results presented in Table II show that our approach converges very

TABLE II. The convergence of the energy and the expectation values of the interparticle distances for the $v = 22$ state with the number of the basis functions. All quantities in atomic units.

Basis size	E	$\langle r_{d-p} \rangle$	$\langle r_{d-e} \rangle$	$\langle r_{p-e} \rangle$	$\langle r_{d-p}^2 \rangle$	$\langle r_{d-e}^2 \rangle$	$\langle r_{p-e}^2 \rangle$
1000	-0.499 864 251 6	24.615	1.6206	24.529	638.88	4.5235	639.96
1500	-0.499 865 746 9	28.590	1.5985	28.523	904.16	4.2421	905.55
2000	-0.499 865 769 2	28.527	1.5999	28.459	900.41	4.2607	901.79
2500	-0.499 865 774 5	28.628	1.5998	28.559	910.11	4.2591	911.49
3000	-0.499 865 776 6	28.619	1.6001	28.551	909.65	4.2650	911.03
3500	-0.499 865 777 1	28.618	1.6002	28.550	909.60	4.2655	910.98
4000	-0.499 865 777 5	28.621	1.6002	28.552	910.00	4.2661	911.37
Ref. 25	-0.499 865 778 5						

well to the best energy value reported for the $v = 22$ state in the literature. Furthermore, the calculations show that with 2000 functions in the basis set the average distances are very well converged. They should be even better converged with that number of basis functions for the lower lying states since those states are easier to describe. The residual difference (by 1 in the ninth decimal) that still remains between our best energy value for the $v = 22$ state obtained with 4000 basis functions and the best literature value can be in part attributed to the incompleteness of the 4000-term basis. However, it may also be a result of the known inability of the Gaussians to describe the electronic and nuclear cusps in the wave function.

To summarize, a rigorous, variational, high-accuracy, nonadiabatic calculation employing explicitly correlated Gaussian basis functions have been performed for the HD^+ ion to determine the degree of charge asymmetry in this system. The results indicate that a catastrophic breakdown of the Born–Oppenheimer approximation occurs above $v = 20$ vibrational level. In the $v = 21$ and $v = 22$ states the electron becomes entirely localized around the deuteron and it is completely absent at the proton. This strong, purely nonadiabatic effect occurs when the dissociation energy of a vibrationally excited state becomes close to the difference between the total energies of the H and D atoms.

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