

Static properties and Stark effect of the ground state of the HD molecular ion

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We have calculated static properties of the ground state of the HD^+ ion and its lowest-lying P-state without making use of the Born-Oppenheimer approximation, as was done in the case of H_2^+ and D_2^+ [Phys. Rev. A **58**, 2787 (1998)]. The ion is treated as a three-body system whose ground state is spherically symmetric. The wavefunction is of generalized Hylleraas type, but it is necessary to include high powers of the internuclear distance to localize the nuclear motion. We obtain good values of the energies of the ground S-state and lowest P-state and compare them with earlier calculations. Expectation values are obtained for various operators, the Fermi contact parameters, and the permanent quadrupole moment. The cusp conditions are also calculated. The polarizability was then calculated using second-order perturbation theory with intermediate P pseudostates. Since the nuclei in HD^+ are not of equal mass there is dipole coupling between the lowest two rotational states, which are almost degenerate. This situation is carefully analyzed, and the Stark shift is calculated variationally as a function of the applied electric field.

I. INTRODUCTION

By observing Rydberg states of HD, it should be possible to extract properties of the HD^+ ion, which is the core of the excited molecule. Such experiments [1] have been performed on Rydberg states of H_2 and D_2 giving highly accurate polarizabilities of H^{\dagger} and D^{\dagger} ions. Our recent calculations



[2] for the polarizabilities of the spherically symmetric ground state of the homonuclear molecular ions agreed very well with the high precision experimental results [1]. We showed that it is possible to avoid the Born-Oppenheimer approximation (BO), which uses a product of electronic and nuclear wave functions, by following the same approach in diatomic molecular systems as has traditionally been used in two-electron atomic systems [3]. We simply treat the molecular ion as a three-body quantum system.

We showed in our previous paper [2] that it is possible to modify the generalized Hylleraas basis functions, which had worked very well in a number of two-electron systems, to apply to two heavy particles and one light particle, thereby treating all three particles on an equal footing. Since no approximations are made (beyond the finite expansion length) in the calculation of eigenvalues by a variational principle, the results obtained, which include the kinematic effects of “rotation” and “vibration” and electron excitation, should be better than in the BO approximation, which assumes that there is no direct coupling between the electronic and nuclear motions. These effects are automatically included when we calculate three-body wave functions.

It is well known that the power-exponential form of a Hylleraas function is well suited to describe the motion of electrons, which are not localized. In order to describe the relative motion of heavy particles which are fairly tightly localized, it is necessary to modify the forms of the functions by introducing very high powers of the distance between the heavy particles. This significantly improves the convergence of the energy values. Using the wave functions obtained by minimizing the energy using the Rayleigh-Ritz variational principle, just as for H_2^+ and D_2^+ [3], we calculate expectation values for various operators, the Fermi contact parameters, the permanent quadrupole moment, and the cusp conditions. The energies obtained are compared with those given by Moss [4].

II. FORMULATION

The unperturbed Hamiltonian of the HD⁺ system is

$$H = -\frac{1}{M_P} \nabla_P^2 - \frac{1}{M_D} \nabla_D^2 - \nabla_e^2 + 2 \left[\frac{1}{|\vec{R}_P - \vec{R}_D|} - \frac{1}{|\vec{R}_P - \vec{R}_e|} - \frac{1}{|\vec{R}_D - \vec{R}_e|} \right] \quad (1)$$

where \vec{R}_P , \vec{R}_D and \vec{R}_e are the position vectors of the proton, deuteron and electron, respectively, measured in units of the Bohr radius a_0 , M_P and M_D are the masses in units of the electron mass, and the energy is in rydbergs. The dipole operator d is defined as

$$d = 2(\vec{R}_P + \vec{R}_D - \vec{R}_e) \cdot \hat{e}, \quad (2)$$

where \hat{e} is a unit vector in the direction of the applied electric field.

We make the usual transformation to the center of mass system:

$$\vec{R}_{CM} = \frac{M_P \vec{R}_P + M_D \vec{R}_D + \vec{R}_e}{M_P + M_D + 1}, \quad \vec{r}_{1,2} = \vec{R}_{P,D} - \vec{R}_e. \quad (3)$$

In terms of these new coordinates, excluding the center-of mass contribution, the Hamiltonian takes the form

$$\bar{H} = -\frac{1}{\mu_P} \nabla_1^2 - \frac{1}{\mu_D} \nabla_2^2 - 2 \vec{\nabla}_1 \cdot \vec{\nabla}_2 + \frac{2}{|\vec{r}_1 - \vec{r}_2|} - \frac{2}{r_1} - \frac{2}{r_2}, \quad (4)$$

and the dipole operator becomes

$$d = 2 \left[\bar{R}_{CM} + \frac{M_D+1}{M_T} \bar{r}_1 + \frac{M_P+1}{M_T} \bar{r}_2 \right] \cdot \hat{e}, \quad (5)$$

where

$$M_T = M_P + M_D + 1, \quad \mu_P = \frac{M_P}{M_P + 1}, \quad \text{and} \quad \mu_D = \frac{M_D}{M_D + 1}. \quad (6)$$

(Notice that in this case the mass polarization cross-term in \bar{H} is of the same order as the other kinetic-energy operators, rather than being small as it is in a two-electron atom like helium.) Numerically, $M_P=1\ 836.152\ 701$ and $M_D=3\ 670.483\ 014$. It is worth emphasizing again that we are treating all three particles on an equal footing and will generally not refer to any special “molecular” quantum numbers except perhaps to clarify the physical situation..

III. CHOOSING THE FUNCTIONS

We are interested in calculating the static properties of the $L=0$ ground state of HD^+ including the binding energy of the ground state, and in order to compute the dipole polarizability it is also necessary to construct a set of pseudostates of orbital angular momentum $L=1$. In the past [5] we have used the following types of Hylleraas functions successfully for these purposes:

$$\Psi_0 = e^{-ar_1 - br_2} e^{-\alpha_s r_{12}} \sum_{lmn=0}^{\Omega_0} c_{lmn} r_1^l r_2^m r_{12}^n \quad (7)$$

$$\text{and } \Psi_p = -\cos(\theta_{12}/2)(f+g)D_1^{1+} - \sin(\theta_{12}/2)(f-g)D_1^{1-} \quad (8)$$

where the radial functions f and g are given by

$$f(r_1, r_2, r_{12}) = e^{-\gamma(r_1+r_2)} e^{-\alpha_p r_{12}} r_1 \sum_{ijk=0}^{\Omega_p} d_{ijk} r_1^i r_2^j r_{12}^k \quad (9)$$

$$\text{and } g(r_2, r_1, r_{12}) = e^{-\gamma(r_1+r_2)} e^{-\alpha_p r_{12}} r_2 \sum_{ijk=0}^{\Omega_p} \bar{d}_{ijk} r_2^i r_1^j r_{12}^k. \quad (10)$$

The rotational harmonics D_1^{+1} and D_1^{-1} used in Eq. (8) are those defined by Bhatia and Temkin [6], and $\bar{r}_{12} = \bar{r}_1 - \bar{r}_2$. In this case there is no exchange between the nuclei and therefore two independent functions are required in Eq. (8) because the electron can be in an L=1 state with respect to the proton or with respect to the deuteron. For convenience in optimization, the nonlinear parameters have been kept the same in the two functions f and g but they could have been chosen different in the two functions.

Although the exponentials and powers appearing in Eqs. (7), (9), and (10) are efficient for describing the correlations between the nuclei and the electron, we know from the BO model (which is certainly a good first approximation) that the internuclear motion will not be well described that way. It is much better described by Gaussian-like functions centered around the equilibrium positions of the nuclei. The problem is to adapt our trial functions so that they describe the motion of the nuclei satisfactorily. The method we use is to increase powers of r_{12} appearing in Eqs. (7), (9),

and (10). This has been illustrated for H_2^+ in Fig. 1 of Ref. [2] which shows that the ground state wave function obtained from the Morse potential [7] can be well approximated by the form $r_{12}^N e^{-\alpha_s r_{12}}$, provided N is large and $\alpha_s \approx N/2$. This leads us to make a simple modification of the trial functions of Eqs. (7), (9), and (10): multiply Eq. (7) by $r_{12}^{N_0}$ and Eqs. (9) and (10) by $r_{12}^{N_p}$.

IV. PROPERTIES OF HD^+

The energy eigenvalues are calculated by the usual Rayleigh-Ritz variational principle which requires minimizing E with respect to variation of the nonlinear parameters in the expression

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (11)$$

Here Ψ can be Ψ_0 or Ψ_p giving E_0 or E_p . For $\Omega_0 = 13$ (560 terms in the expansion), $N_0 = 12$ we obtain $E_0 = -1.195\,795\,889$ Ry which compares well with $-1.195\,795\,931$ Ry obtained by Moss [4], differing by only 4.2×10^{-8} Ry. Similarly, for $L=1$, for $\Omega_p = 11$ (728 terms in Eq. (9)), $N_p = 7$ we obtain the lowest eigenvalue $E_p = -1.195\,371\,602$ Ry which is fairly close to $-1.195\,396\,256$ Ry obtained by Moss [4], but differing this time by 2.5×10^{-5} Ry.

Using the wave functions obtained variationally, expectation values of various quantities are calculated for the ground state as well as the lowest $L=1$ state. They are given in Table I. In the table, \bar{r} represents the distance of the electron from the center of mass of the nuclei and z is the projection of \bar{r} onto \bar{r}_{12} and they are given by the expressions

$$r^2 = \frac{(1+c_3)r_1^2 + (1-c_3)r_2^2}{2} - \frac{(1-c_3^2)r_{12}^2}{4}, \quad (12)$$

$$z \equiv \frac{\bar{r}\bar{r}_{12}}{r_{12}} = \frac{r_1^2 - r_2^2 + c_3 r_{12}^2}{2r_{12}}, \quad (13)$$

and $Q = \frac{1}{2} \langle r_{12}^2 + r^2 - 3z^2 \rangle$ is the permanent quadrupole moment. In Eqs. (12) and (13) $c_3 = \frac{M_P - M_D}{M_P + M_D}$. In the Table energies are in units of Ry, and distances are in units of a_0 . The cusp values with respect to r_1 and r_2 are close to μ_P and μ_D , respectively. The Dirac δ functions $\delta(\bar{r}_1)$ and $\delta(\bar{r}_2)$ required in the calculation of the Fermi contact term are also given in the Table. There does not seem to be another comparable calculation of these properties.

V. POLARIZABILITY

Having established that accurate wave functions can be obtained for the ground as well as the excited states, we can now calculate the dipole polarizability α_1 by ordinary second-order perturbation theory:

$$\alpha_1 = \sum_p \frac{\langle 0|d|p\rangle \langle p|d|0\rangle}{E_p - E_0} a_0^3, \quad (14)$$

where d is the dipole operator defined in Eq. (5), and we can drop the center-of-mass coordinate which has no direct effect on the polarizability. For this purpose we use the ground state wave

function obtained with 560 terms and for intermediate states we keep $N_p = 7$ as we vary Ω_p . Not surprisingly, we find that almost all of the calculated polarizability comes from the lowest-lying p-state in the intermediate sum in Eq. (14). This is due to the very small difference $\Delta_{01} = 4.24287 \times 10^{-4} \text{ Ry}$ between the ground and first excited states. Because the polarizability is so sensitively dependent on this difference we have chosen to replace our calculated value by the more accurate value given by Moss, $\Delta_{01} = 3.996750 \times 10^{-4} \text{ Ry}$. The polarizability due to this single term is then $392.0814 a_0^3$, and the sum over all the remaining intermediate states contributes $3.2076 a_0^3$. The convergence of this second component ($\bar{\alpha}_s$) and the energy of the lowest p-state are displayed in Table II. If the ground state is excluded, there is a corresponding modified spherical polarizability of the lowest p-state ($\bar{\alpha}_p$) due to coupling only with s-states, not d-states. The convergence of this quantity and the energy of the ground state is shown in Table III. The total polarizability, $\alpha = 395.289 a_0^3$, is very much larger than might be expected from the results [1,2],[8] in H_2^+ and D_2^+ . This can be traced to the fact that HD^+ is heteronuclear, and so there is coupling between the ground state and the very low-lying first p-state, which would not happen in the homonuclear cases. We will discuss this situation in detail in the Appendix.

It is essential to remember that the perturbation formula is valid only if the perturbing potential is small compared to the spacing of the unperturbed energy levels. In the homonuclear case this condition is easy to satisfy, since the lowest p-state is not coupled to the ground state, but for HD^+ where there is coupling to the low-lying p-state the calculated polarizability is meaningful only for extremely weak electric fields, much weaker than those found in Rydberg states of the HD molecule. In the next section we will quantify this statement and suggest a way to compute the Stark effect nonperturbatively.

VI. NONPERTURBATIVE CALCULATION OF THE STARK EFFECT

To quantify the applied electric field in terms that are scaled conveniently for the present problem, let the perturbing potential be that of a fixed point (electronic) charge at a large distance R from the molecular ion, so that only the dipole term needs to be retained:

$$V(R) = \frac{d}{R^2}, \quad (15)$$

where d is the dipole operator defined in Eq. (5), and the unit vector $\hat{\epsilon}$ is in the direction of \vec{R} . The matrix element connecting the ground s-state and the lowest, almost degenerate, p-state is calculated to be $M_{01} \equiv \langle 0|d|1\rangle = -0.395860$, and we saw that the energy difference Δ_{01} between these two states is $3.996750 \times 10^{-4} \text{ Ry}$, so R^{-2} is sufficiently small for the perturbation calculation to be valid only when $R^2 \gg 1000$ or $R \gg 32$. This means that for small values of R there are effectively degenerate states of opposite parity, coupled by the dipole operator, and hence giving rise to an energy shift that is linear in the perturbation, rather than quadratic. (This situation occurs most famously in the $2S_{1/2}$ and $2P_{1/2}$ states of hydrogen, whose degeneracy is broken slightly by quantum electrodynamic effects.)

A simple way of constructing a variationally correct approximation to the energy shift of the ground state (the Stark effect) involves only the two lowest opposite parity states. (We have already seen that these produce almost all the asymptotic polarizability.) We write the trial function as

$$|\Psi_2\rangle = C_0|0\rangle + C_1|1\rangle, \quad (16)$$

where 0 and 1 refer to the lowest s and p states, respectively. Then the variational expression for the

total energy has the form

$$E(R) = \frac{\langle \Psi_2 | H_0 + V(R) | \Psi_2 \rangle}{\langle \Psi_2 | \Psi_2 \rangle} = \frac{C_0^2 E_0 + C_1^2 E_1 + 2C_0 C_1 M_{01}/R^2}{C_0^2 + C_1^2}. \quad (17)$$

By varying on the two expansion coefficients in the usual way we obtain the eigenvalue condition

$$\begin{vmatrix} \epsilon(R) & \frac{M_{01}}{R^2} \\ \frac{M_{01}}{R^2} & \epsilon(R) + \Delta_{01} \end{vmatrix} = 0, \quad (18)$$

which gives rise to a quadratic equation whose solution is

$$\epsilon(R) = \frac{\Delta_{01}}{2} \left[\sqrt{1 + 4 \left(\frac{M_{01}}{R^2 \Delta_{01}} \right)^2} - 1 \right] = 1.998375 \times 10^{-4} \left[\sqrt{1 + \frac{3.924002 \times 10^6}{R^4}} - 1 \right], \quad (19)$$

where we have defined the Stark energy shift of the ground state as $\epsilon(R) = E_0 - E(R)$ and have inserted the values previously used for M_{01} and Δ_{01} . In the large-R limit binomial expansion of the square root gives the usual polarizability expression, $\epsilon(R) \approx M_{01}^2 / (\Delta_{01} R^4)$, while for small R we obtain $\epsilon(R) \approx M_{01} / R^2$. To display quantitatively the properties of this adiabatic potential, we plot $\alpha(R) \equiv R^4 \epsilon(R)$ in Fig. 1. This “field-dependent polarizability” goes over to the usual weak-field value of α for large R, including only the lowest p-state as discussed above.

To improve this two-state result in a variationally correct way, we now show two successive corrections which introduce the effects of the perturbation of the two lowest-lying states. First, we

add to the trial function of Eq. (16) an additional term that takes account of the excited p-states:

$$|\Psi_3\rangle = |\Psi_2\rangle + \bar{C}_{sp} \sum_{\bar{p}=1} \frac{V(R)|\bar{p}\rangle \langle \bar{p}|V(R)|0\rangle}{E_0 - E_{\bar{p}}}, \quad (20)$$

where the new term is the perturbation of the ground state, but omitting the lowest p-state. Then we can extend this process one more step by adding the perturbation of the lowest p-state:

$$|\Psi_4\rangle = |\Psi_3\rangle + \bar{C}_{ps} \sum_{\bar{s}=0} \frac{V(R)|\bar{s}\rangle \langle \bar{s}|V(R)|1\rangle}{E_1 - E_{\bar{s}}}. \quad (21)$$

To clarify this method, we define in advance all the quantities that will be needed, some of which have already been used and give their numerical values.

$$\begin{aligned} M_{01} = \langle 1|d|0\rangle &= -0.395860, \quad \Delta_{01} = 3.996750 \times 10^{-4}, \quad \bar{\alpha}_s = \sum_{\bar{p}=1} \frac{\langle 0|d|\bar{p}\rangle \langle \bar{p}|d|0\rangle}{E_{\bar{p}} - E_0} = 3.207642, \\ \bar{\alpha}_p &= \sum_{\bar{s}=0} \frac{\langle 1|d|\bar{s}\rangle \langle \bar{s}|d|1\rangle}{E_{\bar{s}} - E_1} = 2.030078, \quad \bar{\beta}_s = \sum_{\bar{p}=1} \frac{\langle 0|d|\bar{p}\rangle \langle \bar{p}|d|0\rangle}{(E_{\bar{p}} - E_0)^2} = 7.913258, \\ \bar{\beta}_p &= \sum_{\bar{s}=0} \frac{\langle 1|d|\bar{s}\rangle \langle \bar{s}|d|1\rangle}{(E_{\bar{s}} - E_1)^2} = 9.136986, \quad Q_3 = \sum_{\bar{s}=0, \bar{p}=1} \frac{\langle 0|d|\bar{p}\rangle \langle \bar{p}|d|\bar{s}\rangle \langle \bar{s}|d|1\rangle}{(E_{\bar{s}} - E_1)(E_{\bar{p}} - E_0)} = -6.120350. \end{aligned} \quad (22)$$

In the evaluation of these sums, 560 intermediate s-states and 728 p-states were retained, with the exception of the double sum in Q_3 , where only 120 s-states and 240 p-states were included.

If we insert the 3- or 4-term trial functions in place of $|\Psi_2\rangle$ in Eq. (17) and vary on all the coefficients, we will obtain a determinantal secular equation for the expectation value of the Stark energy shift $\epsilon(R)$. For the four-term approximation we find the following form:

$$\begin{vmatrix}
 \epsilon(R) & \frac{M_{01}}{R^2} & -\frac{\bar{\alpha}_s}{R^4} & 0 \\
 \frac{M_{01}}{R^2} & \epsilon(R) + \Delta_{01} & 0 & -\frac{\bar{\alpha}_p}{R^4} \\
 -\frac{\bar{\alpha}_s}{R^4} & 0 & \frac{\bar{\beta}_s \epsilon(R) + \bar{\alpha}_s}{R^4} & \frac{Q_3}{R^6} \\
 0 & -\frac{\bar{\alpha}_p}{R^4} & \frac{Q_3}{R^6} & \frac{\bar{\beta}_p [\epsilon(R) + \Delta_{01}] + \bar{\alpha}_p}{R^4}
 \end{vmatrix} = 0 \quad (23)$$

(This determinant evidently includes the 2x2 and 3x3 subdeterminants appropriate for the other two expansion lengths.) In Fig. 2 we have plotted the differences $\alpha_{3,4}(R) - \alpha_2(R)$ between the field-dependent polarizability in each of these two expanded approximations and that of the simple 2-term value plotted in Fig. 1. As expected from the construction of the 3- and 4-term trial functions, this difference goes asymptotically to $\bar{\alpha}_s$, the contribution to the polarizability of the ground state coming from all intermediate p-states except the lowest one. For other values of R the 4-term result is greater than the 3-term result, since they are both variationally correct.

These curves are the main results of the present work, and they give an effective, R -dependent polarizability (or Stark shift) that is a lower bound to the true value. Strictly speaking, since this is only a static energy shift it is not directly applicable to the experimental problem of the Rydberg states of the HD molecule itself, and it is likely that non-adiabatic corrections and higher-multipole contributions will be very large. (We intend to investigate such effects in the future.) But it is still interesting to see the effect of the best potential calculated here on a set of Rydberg levels. To do this, we simply computed the expectation value

$$\Delta E_{NL} = - \int \Psi_{NL}(R) \epsilon_4(R) \Psi_{NL}(R) d^3R, \quad (24)$$

using hydrogen wave functions. The results (in MHz) are shown in Table IV; they are, as expected, quite large.

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APPENDIX

In this work we found it necessary to take account of the near-degeneracy of the two lowest states of opposite parity, which contribute the majority of the dipole polarizability in the weak-field regime, and are significantly involved in the Stark effect as the electric field increases. One may reasonably ask whether higher rotational levels, also of alternating parity, may be important as well.

The first answer is that since only $L=1$ states contribute to the perturbation of the $L=0$ ground state, there is no effect on the asymptotic polarizability. But as the field increases and higher-order couplings begin to appear these higher- L states should be important. In fact, we intend to extend the present research to these higher angular momentum states, but for the moment we describe an approximate calculation that shows semiquantitatively that such states are not insignificant.

Let us introduce a rigid rotor model from which we can calculate energy differences and dipole matrix elements between the low-lying rotational states. A good approximation is to assume that the electron spends about half the time in a hydrogenic state centered on each of the two nuclei. Then the rotational energy of each state can be approximated as

$$\Delta_{0L} = \frac{L(L+1)}{2} \left(\frac{1}{\bar{\mu}_D} + \frac{1}{\bar{\mu}_P} \right) \left\langle \frac{1}{r_{12}^2} \right\rangle = 1.996745 \times 10^{-4} L(L+1) Ry, \quad (25)$$

where $\bar{\mu}_{D,P} \equiv \frac{M_{D,P}(M_{P,D} + 1)}{M_P + M_D + 1} = [1224.3435, 1224.0104],$

and where we have used the data from Table I to evaluate the expectation value and averaged over the two configurations. For the energy difference used previously this formula gives $\Delta_{01} = 3.993491 \times 10^{-4} Ry$, in almost exact agreement with the accurate result of Moss that we have used in our numerical calculations. We will continue to use this expression for the higher L states, although we are aware that there are small centrifugal stretching corrections that should be included.

To calculate the dipole operator in this model, we assume again that there are two terms, and that in each one there is a neutral atom (either D or H) and an ion, separated by a distance $\langle r_{12} \rangle$. The contribution from each of these configurations is given by the vector from the center of mass to the charged particle. In this way we find the following expression for the dipole operator:

$$d = \frac{M_D - M_P}{M_D + M_P + 1} \langle r_{12} \rangle \cos\theta = 0.684758 \cos\theta, \quad (26)$$

where we have used the value of $\langle r_{12} \rangle$ from Table I, averaged over the lowest s and p states, and θ is the angle between the applied electric field and the internuclear axis. (Incidentally, this formula shows explicitly why there is no dipole coupling between the low-lying rotational states for homonuclear ions.) Then the dipole matrix element between two neighboring rotational states in this model is

$$M_{LL+1} = M_{L+1L} = 0.684758 \int d\Omega Y_L^0(\Omega) \cos\theta Y_{L+1}^0(\Omega) = 0.342379 \sqrt{1 + \frac{1}{4L^2 + 8L + 3}}. \quad (27)$$

For the matrix element connecting the two lowest rotational states this formula gives the value $M_{01} = 0.395345$, in excellent agreement with our numerical result. The good agreement both of the energy spacing and the dipole matrix element, at least for the first two levels, supports the use of this simple model to calculate the Stark effect.

To evaluate the field-dependent polarizability of HD^+ with this model, we extend the variational trial function of Eq. (16) to include more rotational states. For concreteness we will include a total of five. The secular determinant corresponding to Eq. (18) has elements of the following general form:

$$F_{ij} = [\epsilon(R) + \Delta_{0j-1}] \delta_{ij} + \frac{M_{i-1j-1}}{R^2} [\delta_{ij+1} + \delta_{ij-1}], \quad 1 \leq i, j \leq 5. \quad (28)$$

By setting the secular determinant to zero we obtain improved values of the energy shift and thus the field-dependent polarizability that are almost rigorously variational. In Fig. 3 the effect of including first the $L=2$ state and then the $L=3$ state is shown. As expected, the polarizability is noticeably

increased for intermediate values of R , while the asymptotic polarizability is not affected at all. Adding one more term does not make a significant change.

We expect to find very similar, but more rigorous, results when we carry out a full variational calculation including angular momentum terms with $L > 1$ in the trial function.

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1 lowest P-state energies and expectation values of various operators for HD⁺.

Quantity	Ground State	Lowest P State
E	-1.195 795 889	-1.195 371 602
cusps(r_1)	-0.9987104	
$\langle \delta(r_1) \rangle$	0.207 300 621	
cusps(r_2)	-0.999832	
$\langle \delta(r_2) \rangle$	0.207 350 189	
$\langle r_{12}^4 \rangle$	19.017 155	19.132 500
$\langle r_{12}^3 \rangle$	8.962 068	9.004 201
$\langle r_{12}^2 \rangle$	4.268 373	4.279 340
$\langle r_{12} \rangle$	2.054 808	2.057 208
$\langle 1/r_{12} \rangle$	0.492 058	0.491 595
$\langle 1/r_{12}^2 \rangle$	0.244 844	0.244 437
$\langle r_1^4 \rangle$	23.678 744	23.761 923
$\langle r_1^3 \rangle$	8.619 449	8.641 534
$\langle r_1^2 \rangle$	3.536 574	3.542 320
$\langle r_1 \rangle$	1.688 444	1.689 706
$\langle 1/r_1 \rangle$	0.843 715	0.843 272
$\langle r_2^4 \rangle$	23.646 990	23.730 014
$\langle r_2^3 \rangle$	8.610 227	8.632 275
$\langle r_2^2 \rangle$	3.533 853	3.539 591
$\langle r_2 \rangle$	1.687 735	1.689 027
$\langle 1/r_2 \rangle$	0.844 139	0.843 697
$\langle r_1 r_2 \rangle$	2.794 177	2.797 744
$\langle \cos \theta_{12} \rangle$	0.253 063	0.252 710
$\langle r^2 \rangle$	2.586 076	2.589 379

$\langle r_1^2 r_2^2 / r_{12}^2 \rangle$	3.143 535	3.157 374
$\langle r_1^4 / r_{12}^2 \rangle$	5.486 286	5.490 379
$\langle r_2^4 / r_{12}^2 \rangle$	5.480 773	5.484 856
$\langle z^2 \rangle^a$	1.280 997	1.283 381
Q^b	1.505 729	1.509 289
$\langle \nabla_1^2 \rangle$	-5.980 024	
$\langle \nabla_2^2 \rangle$	-5.982 278	
$\langle \nabla_1 \cdot \nabla_2 \rangle$	5.385 369	

$$^a \bar{r} = \frac{\vec{r}_1 + \vec{r}_2}{2} + \frac{M_P - M_D}{2(M_P + M_D)} \vec{r}_{12} \quad \text{and} \quad z = \frac{\vec{r} \cdot \vec{r}_{12}}{r_{12}}$$

$$^b Q = \frac{1}{2} \langle r_{12}^2 + r^2 - 3z^2 \rangle \text{ is the permanent quadrupole moment.}$$

Table II. The convergence of the lowest p-state energy and $\bar{\alpha}_s$ as a function of Ω_p , using the best-converged form of the ground-state wave function ($\Omega_s=13$).

Ω_p	$2N^a$	E^b	$\bar{\alpha}_s$
5	112	-1.194 238 824 84	3.089 392 245 14
6	168	-1.194 801 771 34	3.133 695 375 18
7	240	-1.195 030 443 09	3.162 882 250 62
8	330	-1.195 230 047 56	3.184 864 200 87
9	440	-1.195 322 697 52	3.196 669 457 93
10	572	-1.195 364 513 31	3.203 457 222 84
11	728	-1.195 371 601 84	3.207 641 745 15

^a $2N$ represents the number of terms retained in the expansion.

^b E is the energy of the lowest $L=1$ state.

Table III. The convergence of $\bar{\alpha}_p$ and the ground-state energy as functions of Ω_s , using the best-converged form of the lowest p-state wave function ($\Omega_p = 11$).

Ω_s	N^a	E^b	$\bar{\alpha}_p$
7	120	-1.195 786 258 30	2.023 780 342 07
8	165	-1.195 791 941 57	2.027 828 656 13
9	220	-1.195 794 053 97	2.028 761 648 12
10	286	-1.195 794 976 73	2.029 306 062 83
11	364	-1.195 795 415 58	2.029 653 261 48
12	455	-1.195 795 633 82	2.029 917 067 13
13	560	-1.195 795 888 91	2.030 078 303 37

^a N represents the number of terms retained in the expansion

^b E is the energy of the lowest S state.

Table IV. Effective potential \bar{V}_{NL} obtained by averaging $\epsilon(R)$ over hydrogen wave functions, and the effective polarizability defined by $\bar{\alpha}_{NL} \langle 1/R^4 \rangle = \bar{V}_{NL}$.

N	L	$-\bar{V}_{NL}$ (10^5 MHz)	$\bar{\alpha}_{NL}$ (a_0^3)
5	4	18.261	109.52
6	4	9.7218	90.68
	5	6.6838	195.93
7	4	5.8369	81.53
	5	3.9335	166.15
	6	2.5334	278.22
8	4	3.8063	76.54
	5	2.5484	151.57
	6	1.6517	247.56
	7	0.98714	336.26
9	4	2.6302	73.51
	5	1.7572	143.24
	6	1.1462	231.04
	7	0.70289	313.79
	8	0.40172	368.53
10	4	1.8974	71.53
	5	1.2668	137.96
	6	0.83071	220.91
	7	0.51793	300.1
	8	0.30517	355.59
	9	0.17338	383.84

FIGURE CAPTIONS

FIG. 1. Field-dependent polarizability $\alpha_2(R)$ of HD^+ from Eq. (19). The result includes only the two lowest states of opposite parity. The dotted line represents the total asymptotic polarizability, $\alpha = 395.289a_0^3$.

FIG. 2. Polarizability differences $\alpha_3(R) - \alpha_2(R)$ (lower curve) and $\alpha_4(R) - \alpha_2(R)$ (upper curve). These are solutions of the secular Eq. (23) and its subdeterminants. The dotted line represents the asymptotic contribution to the polarizability, $\bar{\alpha}_s = 3.2076a_0^3$.

FIG. 3. Polarizability differences from $\alpha_2(R)$ due to the inclusion of higher rotational states in the model described in the Appendix. The lower curve includes $L=2$, and the upper curve also includes $L=3$, and they result from solving the secular determinant with elements given in Eq. (28). Inclusion of $L=4$ has an insignificant effect.

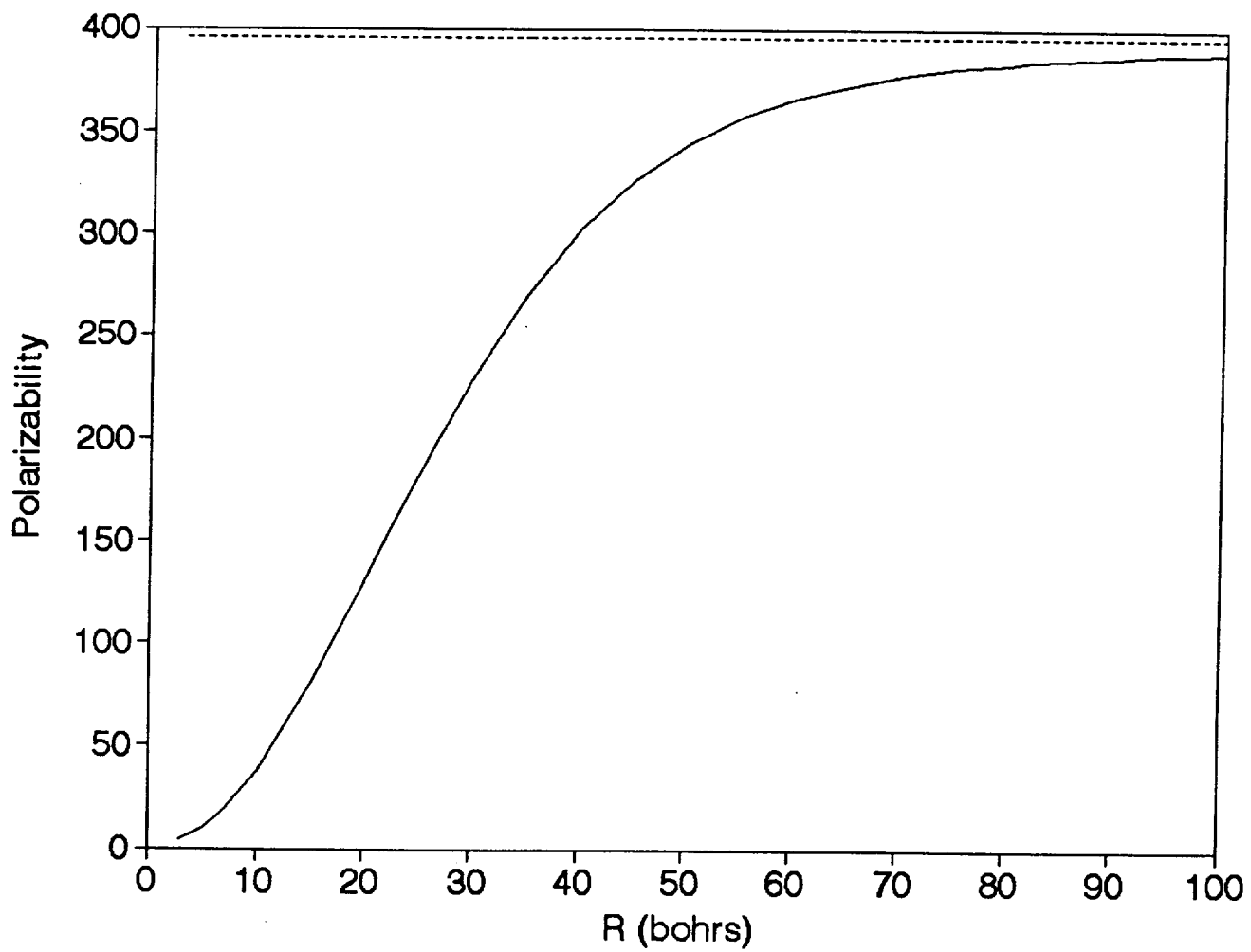


FIG. 1

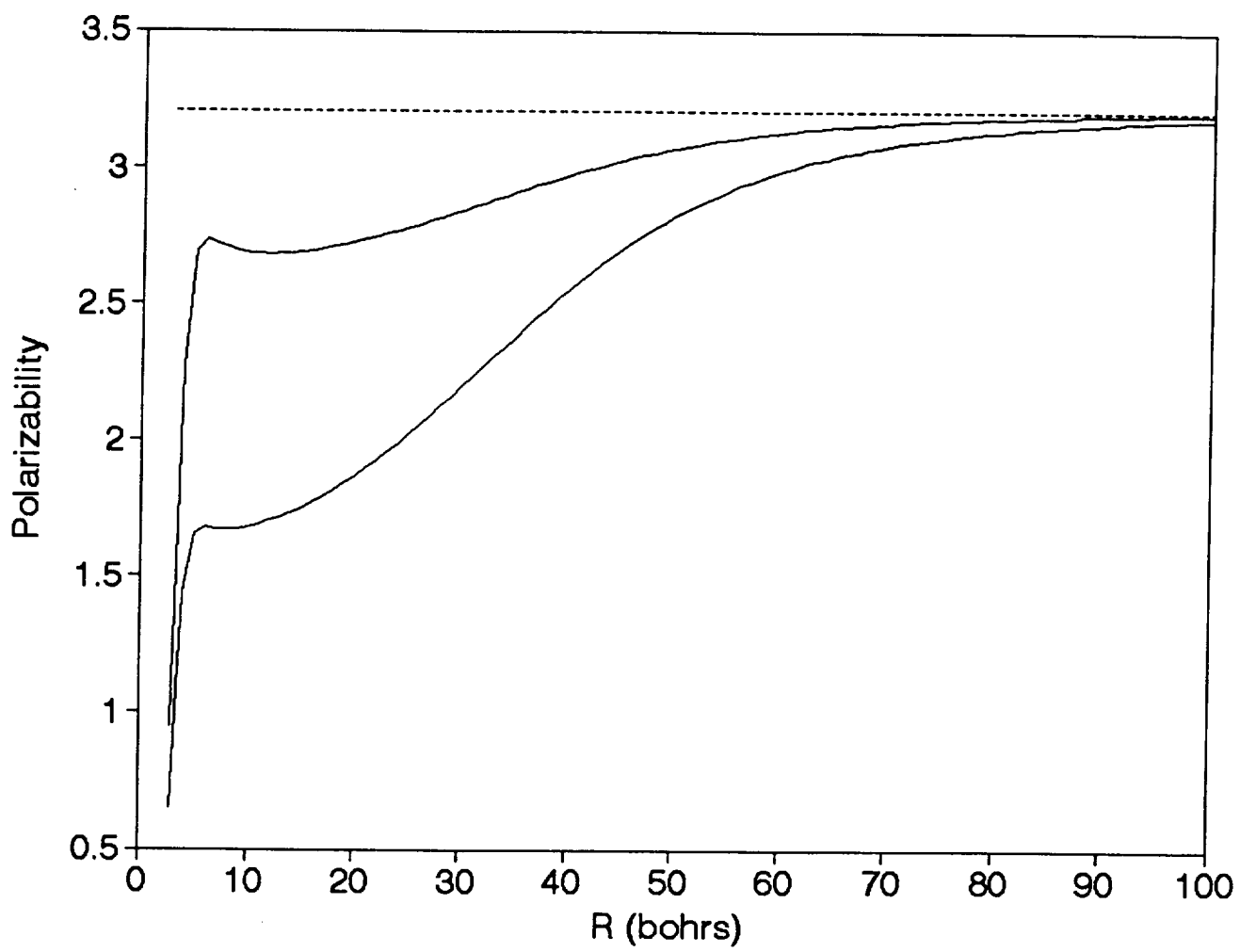


FIG. 2

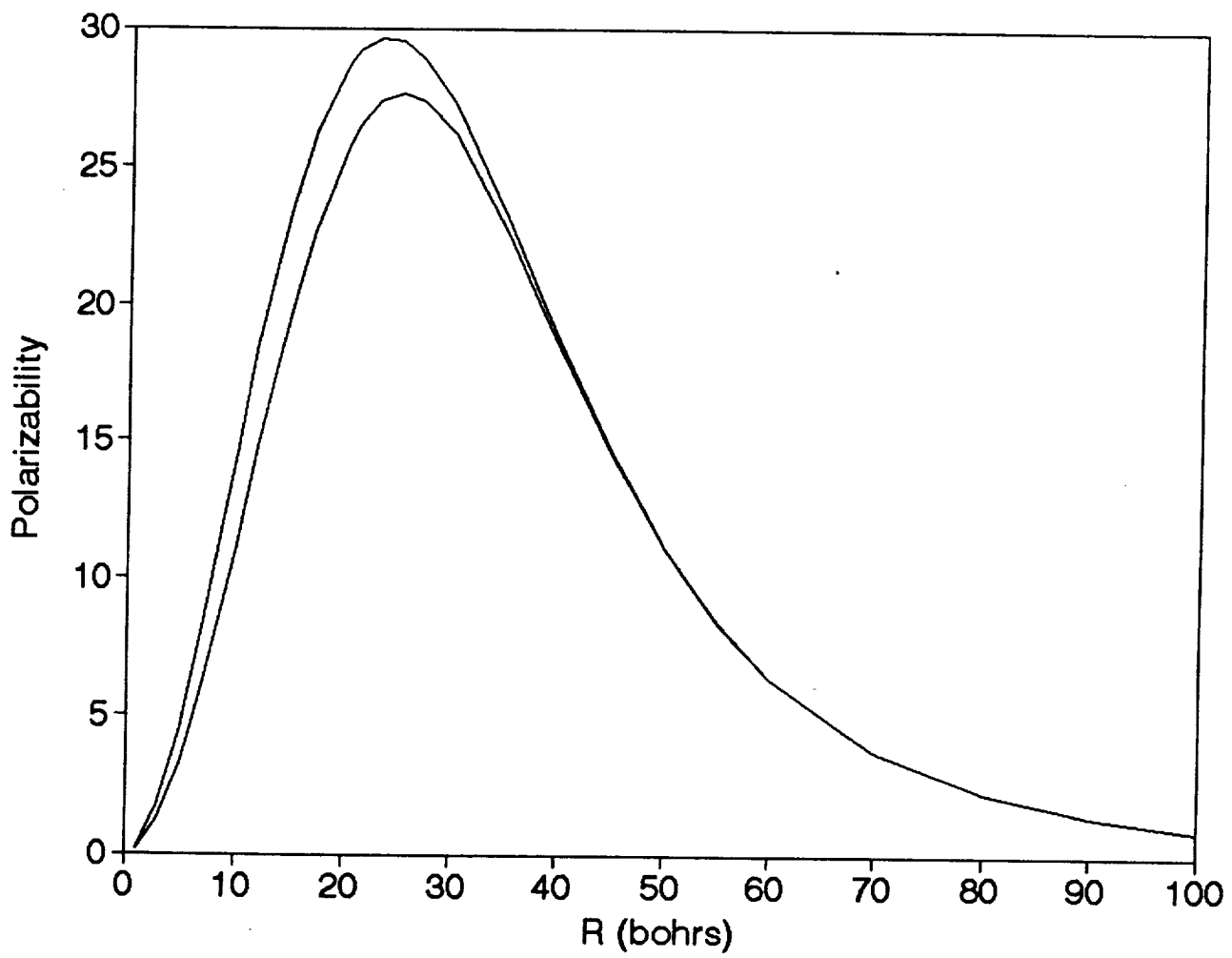


FIG. 3