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Polarizability of the ground state of the hydrogen molecular ion

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The dipole polarizabilities of the ground states of the ions $H_2{}^+$ and $D_2{}^+$ have been calculated without making use of the Born-Oppenheimer approximation. Instead, the ions were treated as three-body systems whose ground states are spherically symmetric, and the polarizabilities were calculated using second-order perturbation theory with intermediate *p* pseudostates. The wave functions of both the ground and intermediate states are taken to be of generalized Hylleraas form, but it is necessary to use quite high powers of the internuclear coordinate to simulate the localized motion of the nuclei. We obtain good values of the ground-state energies, and report values of the polarizabilities, to be compared with recent measurements. [S1050-2947(99)02001-6]

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I. INTRODUCTION

Recent experiments [1] on high Rydberg states of H_2 have made it possible to extract accurate properties of the molecular ion $H_2{}^+$, which is the core of the excited molecule. Among the properties measured are the quadrupole moment and the parallel and perpendicular polarizabilities. More recently, Rydberg states of H_2 and D_2 have been observed, with the core in its spherically symmetric ground state [2], and the isotropic dipole polarizabilities have been determined with high precision. The traditional theoretical values [3] of these polarizabilities have been obtained from averages, over rotational and vibrational wave functions, of quantities calculated in the Born-Oppenheimer (BO) approximation, and they disagree significantly with experiments (see Table I). In the present paper we avoid this approximation by treating the $H_2{}^+$ molecular ion as a three-body quantum system, and computing the polarizability by second-order perturbation theory.

To do this we adapt the generalized Hylleraas basis functions that had worked very well in previous calculations for the atomic helium system and a number of two-electron atomic ions [4]. At first sight this may seem to be a bizarre way to deal with a molecule whose structure is so different qualitatively from a two-electron atom: instead of having one heavy particle and two light ones, $H_2{}^+$ contains two heavy particles and one light one. In principle, however, there is no real reason why it should not be possible to treat all three-particle systems on an equal footing. In fact, a well-converged variational calculation should give better results than the BO method, since no fundamental approximation has been made. The major advantage of treating a diatomic ion as an ordinary three-body system lies in the fact that all the kinematic effects of ''rotation'' and ''vibration'' (as they would be called in the BO method) are automatically included when we calculate the three-body wave functions. By the same token we will not be able to compute separate values of the axial and transverse polarizabilities, since we do not hold the internuclear axis fixed in space. (From this point of view it would be just as silly to ask for the polarizability of the helium atom along the interelectronic direction.) But it is not just the simplicity and straightforwardness of the method that recommends it; there are discrepancies between the best BO calculations [3] and the recent measurements [2], and we hope that these can be cleared up.

The problem is simply one of adequate convergence. It is well known that although the power-exponential form of a Hylleraas function is well suited to describing electronic motions, the relative motion of the nuclei is fairly tightly localized near an equilibrium point; the heavier the nuclei, the more localized their motion becomes. An important part of this work is a simple method to overcome this problem. Nevertheless, convergence in this calculation is still rather slow, especially in the case of $D_2{}^+$; we will discuss this below.

In Sec. II the formulation of the calculation is described, in Sec. III the choice of trial functions is discussed, and in Sec. IV results and extrapolated results are shown.

II. FORMULATION

The unperturbed Hamiltonian of the $H_2{}^+$ system is

$$H=-\frac{1}{M}\left[\nabla_A^2+\nabla_B^2\right]-\nabla_e^2+2\left[\frac{1}{|\vec{r}_A-\vec{r}_B|}-\frac{1}{|\vec{r}_A-\vec{r}_e|}-\frac{1}{|\vec{r}_B-\vec{r}_e|}\right], \qquad (1)$$

TABLE I. Polarizabilities of $H_2{}^+$ and $D_2{}^+$ obtained in different ways, both theoretically and experimentally. Quantities in parentheses are errors in the last decimal place given; estimated errors of the present calculation are shown in Eq. (11).

Method	$\alpha_1(H_2{}^+)$	$\alpha_1(D_2{}^+)$
Experiment[a]	3.1681(7)	3.0712(7)
Born-Oppenheimer[b]	3.1713	3.0731
Present	3.1680	3.0671
Finite element[c]	3.1682(4)	3.0714(4)

[a] Jacobson *et al.* [2].
[b] Bishop and Lam [3].
[c] Shertzer and Greene [10].

where $\vec{r}_A$, $\vec{r}_B$, and $\vec{r}_e$ are the position vectors of the two nuclei and the electron, respectively, measured in units of the Bohr radius a_0, M is the nuclear mass in units of the electron mass, and the energy is in rydbergs. The dipole polarizability (in units of a_0^3) is obtained by second-order perturbation theory as

$$\alpha_1=4\sum_p \frac{|\langle 0|(\vec{r}_A+\vec{r}_B-\vec{r}_e)\cdot\hat{\varepsilon}|p\rangle|^2}{E_p-E_0}. \tag{2}$$

We make the usual transformation to the center of mass system, where

$$\vec{R}_{\mathrm{CM}}=\frac{M\vec{r}_A+M\vec{r}_B+\vec{r}_e}{2M+1},\quad \vec{\rho}_{A,B}=\mu[\vec{r}_{A,B}-\vec{r}_e]. \tag{3}$$

In terms of these new coordinates, the Hamiltonian takes the form

$$\overline{H}=-\nabla^2_{\rho_A}-\nabla^2_{\rho_B}-2\mu\vec{\nabla}_{\rho_A}\cdot\vec{\nabla}_{\rho_B}+\frac{2}{|\vec{\rho}_A-\vec{\rho}_B|}-\frac{2}{\rho_A}-\frac{2}{\rho_B}, \tag{4}$$

and the dipole operator becomes

$$\left[\vec{R}_{cm}+\frac{1}{\mu(1+\mu)}(\vec{\rho}_A+\vec{\rho}_B)\right]\cdot\hat{\varepsilon}, \tag{5}$$

where the reduced mass $\mu=M/(M+1)$, and energies are now measured in reduced rydbergs, $R_\mu=\mu R_\infty$. The center-of-mass term can be omitted since it does not contribute to the polarizability. Nevertheless, the fact that the ion is charged and accelerates in the external field contributes to the coefficient appearing in the dipole operator. (Notice that in this case the mass polarization cross-term in $\overline{H}$ 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.) Finally, we can write the polarizability in the following form:

$$\alpha_1=\frac{4}{\mu^3(1+\mu)^2}\sum_p \frac{|\langle 0|z_A+z_B|p\rangle|^2}{E_p-E_0}a_0^3, \tag{6}$$

where $z_{A,B}=\vec{\rho}_{A,B}\cdot\hat{\varepsilon}$, 0 signifies the spherically symmetric ground state of the ion, and p denotes the excited $L=1$ states. It is worth emphasizing again that we are treating all three particles on an equal footing and will not refer to any special ''molecular'' quantum numbers. Thus we will not be interested here in the ''axial'' or ''transverse'' polarizabilities that appear in BO calculations.

III. CHOOSING THE FUNCTIONS

In the past, we have calculated atomic polarizabilities using S-wave Hylleraas trial functions to describe the unperturbed state, and P-wave Hylleraas functions used as pseudostates to approximate the intermediate-state sum in Eq. (6):

$$\Psi_0=e^{-a(\rho_A+\rho_B)}e^{-b\rho_{AB}}\sum_{l,m,n=0}^{\Omega_0}C_{l,m,n}\rho_A^l\rho_B^m\rho_{AB}^n+[A\leftrightarrows B]. \tag{7}$$

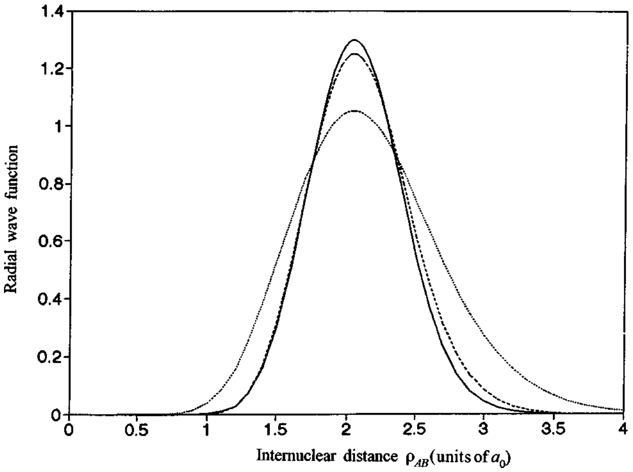

FIG. 1. Demonstration of the similarity between functions of the form $\rho^N e^{-b\rho}$ and solutions of the Morse oscillator for $H_2{}^+$. The solid line is the Morse function, the dotted line is for $N=16$ and $b=7.843\,127$, and the dashed line is for $N=32$ and $b=15.686\,25$. All three functions are normalized to unity.

$$\Psi_p=-\cos(\theta_{AB}/2)(f+\overline{f})D_1^{1+}-\sin(\theta_{AB}/2)(f-\overline{f})D_1^{1-},$$

where

$$f(\rho_A,\rho_B,\rho_{AB})=e^{-\gamma(\rho_A+\rho_B)}e^{-\delta\rho_{AB}}\rho_A\sum_{i,j,k=0}^{\Omega_p}C_{i,j,k}\rho_A^i\rho_B^j\rho_{AB}^k, \tag{8}$$

and

$$\overline{f}(\rho_A,\rho_B,\rho_{AB})=f(\rho_B,\rho_A,\rho_{AB}).$$

The rotational harmonics D used here are those defined by Bhatia and Temkin [5], and $\vec{\rho}_{AB}=\vec{\rho}_A-\vec{\rho}_B$.

Although the exponentials and powers appearing in Eqs. (7) and (8) are efficient for describing the correlation 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 the powers of ρ_{AB} appearing in Eqs. (7) and (8).

In Fig. 1 we show the ground-state wave function obtained from the Morse potential [6], an approximation to the exact BO potential for the $H_2{}^+$ ion. Notice that it peaks just beyond $\rho_{AB}=2a_0$ and has a half-width of about $1a_0$. This function can be well approximated by the form $\rho^N e^{-b\rho}$, provided N is large, and $b\approx N/2$. In the figure we show the two functions $N=16$, $b=7.8431$ and $N=32$, $b=15.6863$. The latter (normalized to unity) fits almost perfectly, while the former is broader but qualitatively similar. (For the case of $D_2{}^+$, where the half-width is smaller, the required value of N is considerably higher, causing a decreased accuracy in treating this system.) This leads us to make a simple modification of the trial functions of Eqs. (7) and (8)—multiplying them by ρ_{AB}^N. For the ground state the nonlinear parameters are chosen to minimize the energy, as usual, but how should the

TABLE II. The convergence of α_1 as a function of Ω_P for both H_2^+ and D_2^+. In both cases $\Omega_0=13$ ($N_0=308$).

Ω_P	N_P	$\alpha_1(H_2)$	$\alpha_1(D_2)$
4	35	3.023 925	2.753 082
5	56	3.094 272	2.904 720
6	84	3.130 915	2.971 445
7	120	3.149 851	3.012 308
8	165	3.159 469	3.037 802
9	220	3.164 864	3.054 261
10	286	3.167 134	3.060 808
11	364	3.167 953	3.067 089

value of N be chosen? We found in practice that an efficient and tractable scheme was to keep $N+\Omega_0$ constant as we increased Ω_0 itself. This has the effect of starting with a function roughly like that shown in Fig. 1, and gradually filling in the lower powers of ρ_{AB} as the expansion length increases. In this way we have obtained a value of the ground-state energy $E(H_2^+)=-1.194\,277\,909$ Ry, differing by only about 2.2×10^{-7} Ry from the accurate value [7]. It is important to emphasize that this procedure is *not* intended to produce a wave function exactly like the BO function. We are simply trying to adjust the form of the conventional Hylleraas trial function to simulate the physics of the BO function qualitatively, by localizing the nuclei close to their most probable positions in the expectation that this will improve convergence, as indeed it does. Notice also that not every term in the expansion has exactly the same dependence on the internuclear coordinate, since various values of n are summed over. Our comparison with the Morse solution in Fig. 1 is not supposed to be quantitative.

For the intermediate p states, on the other hand, we have kept $N=4$, and have chosen the parameters to maximize the value of α_1 as obtained from Eq. (6), following Bishop and Lam [8]. That is, if $|0\rangle$ were the exact ground-state function, then the polarizability obtained from Eq. (6) would be variationally correct and would have errors of second order in the error in the set of p-state functions included in the summation. It would also give a rigorous lower bound, and this is the reason why we choose the p-state parameters to maximize α_1. However, the error that remains in the approximate ground-state function contributes a first-order error to the calculation of α_1, through the matrix element appearing in the numerator.

IV. RESULTS AND DISCUSSION

In Table II we show how our results vary as we increase the number of intermediate p-states for both molecular ions, keeping Ω_0 fixed at 13. The ''best'' values of the polarizabilities, that is, those obtained with the greatest expansion lengths in both the ground state and the intermediate pseudostates, are $\alpha_1(H_2^+)=3.167\,95a_0^3$, and $\alpha_1(D_2^+)=3.067\,09a_0^3$. These should be compared with the corresponding experimental results shown in Table I.

In estimating the accuracy of these numbers, there are two different convergence processes that must be considered: convergence of the ground-state wave function with respect to Ω_0, and convergence of the polarizability with respect to the length of the intermediate p-pseudostate sum, measured by Ω_p. As we discussed above, if the ground-state function were exact, then the convergence in Ω_p would certainly be from below, and in practice we do find convergence of α_1 from below for each value of Ω_0, so it is reasonable to take the two values of the polarizability given above to be lower bounds to the exact values, but these are not rigorous bounds. For the maximum value $\Omega_0=13$ and $N=10$ we find that α_1 converges exponentially with Ω_p

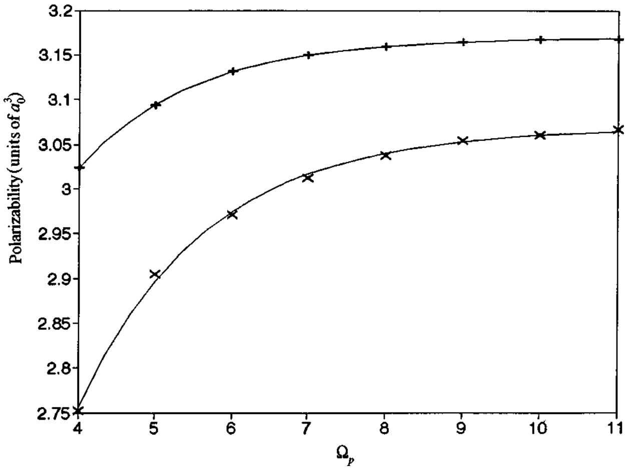

FIG. 2. Convergence of α_1 with $\Omega_0=13$ ($N_0=308$) as a function of Ω_p. The upper curve is for H_2^+, and the lower is for D_2^+.

$$\alpha_1(\Omega_p)=\alpha_1+Ce^{-D\Omega_p}, \tag{9}$$

and this equation actually fits very well for the H_2^+ case and fairly well for D_2^+, as shown in Fig. 2. It is tempting to try to extract a better value of α_1 by taking Eq. (9) literally and using it to extrapolate to $\Omega_p\to\infty$. The two curves shown in Fig. 2 were obtained by least-squares fitting to all the calculated points, and they lead to extrapolated values $\alpha_1(H_2^+)=3.1698(3)a_0^3$, and $\alpha_1(D_2^+)=3.0687(44)a_0^3$. The errors, indicated in parentheses, represent the inadequacy of the exponential form to describe the data; it is clear both numerically and by inspection that the D_2^+ data fit significantly less well. It might be reasonable to take these extrapolated values to be upper bounds [9].

On the other hand, adding terms to the ground-state function decreases the calculated polarizability. This observation is physically reasonable, since as the system becomes more tightly bound it should be more difficult to distort it. To obtain an idea of how much the polarizability would decrease if Ω_0 could be raised indefinitely, we can use the energy error as a measure. The energy error is quadratic in the ground-state wave function error, while the polarizability does not have the variational property; thus we assume the relation

$$\alpha_1(\Omega_0)=\alpha_1+C[E(\Omega_0)-E_{\text{exact}}]^{1/2}, \tag{10}$$

and use the calculated values for $\Omega_0=12$ and 13 to estimate the converged value of the polarizability for fixed value of $\Omega_p=11$ as $\Omega_0\to\infty$. This procedure results in a decrease of

10^{-4} for the case of the hydrogen ion, and 2.0×10^{-3} for the deuterium ion. We can then present the final results in the following forms:

$$\alpha_1(\mathrm{H_2}^+)=3.1680^{+0.0018}_{-0.0001},$$
$$\alpha_1(\mathrm{D_2}^+)=3.0671^{+0.0016}_{-0.0020}. \qquad (11)$$

It is unfortunate that the two expansions converge in opposite directions, making it difficult to obtain more rigorous upper or lower bounds on the polarizability, but the value given above is not inconsistent with the result for $\mathrm{H_2}^+$ obtained in Ref. [2], while the result for $\mathrm{D_2}^+$ is less satisfactory.

The fact that that the convergence of the more massive of the two ions is the poorer of the two may be surprising to those who are used to the BO approximation, where errors depend on the ratio of electron mass to nuclear mass. It is important to remember that the present calculation starts at the other end of the mass ratio scale, and it becomes more and more difficult to apply our method as the nuclear mass increases. The reason why this happens has to do with the increasing difficulty of generating a well-enough localized two-nucleus part of the trial function. Clearly, in the limit of infinite nuclear mass, when the nuclei are stationary, our trial function will be completely incapable of representing the situation, and this inability is already becoming evident for $\mathrm{D_2}^+$. (A recent calculation [10] of the same quantities uses the finite element method, avoids the basis-set problem, and obtains excellent results in good agreement with experiment; see Table I.) It is rather interesting that the boundary between applicability and inappropriateness of our method should be so close to the physically relevant systems considered here. We are currently investigating the polarizabilities of the whole family of three-particle systems, from H^- through $\mathrm{T_2}^+$.

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[9] We also tried an exponential fit with respect to N_p instead of Ω_p. The overall fit is fairly poor, but if we restrict it to the last five values a satisfactory fit is obtained with an extrapolated value of $\alpha_1(\mathrm{H_2}^+)=3.168\,32(7)a_0^3$. We prefer the more conservative results presented above.

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