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Dipole polarizability of the hydrogen molecular ion

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A procedure is described for the precise nonrelativistic evaluation of the dipole polarizabilities of $H_2{}^+$ and $D_2{}^+$ that avoids any approximation based on the size of the electron mass relative to the nucleus mass. The procedure is constructed so that sum rules may be used to assess the accuracy of the calculation. The resulting polarizabilities are consistent with experiment within the error bars of the measurements and are far more precise than values obtained by other theoretical methods. [S1050-2947(99)50710-5]

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The separation of nuclear and electronic motion is the underlying principle of the theory of molecular structure. The theory is challenged by recent measurements of Jacobson *et al.* [1] of the electric-dipole polarizabilities of $H_2{}^+$ and $D_2{}^+$, which have a precision beyond that obtained in the Born-Oppenheimer approximation. The measurements stimulated the introduction of methods [2–5] that take into account the diabatic coupling omitted in the earlier calculations and they led to polarizabilities that agree with the measured values within the combined experimental and theoretical uncertainties. We present here theoretical predictions of much greater accuracy, which in turn pose a significant challenge to experiment. The accuracy of our method can be assessed by the use of sum rules and we predict nonrelativistically the polarizabilities of $H_2{}^+$ and $D_2{}^+$ to a precision well beyond that achieved by the experiments. The method is general and it should be possible to apply it to many-electron diatomic molecules.

Separating out the center-of-mass motion we may write for the Hamiltonian of $H_2{}^+$ or $D_2{}^+$ in an electric field $\mathbf{F}=F\hat{\boldsymbol{n}}$ lying along the Z axis of the space-fixed frame,

$$H=-\frac{1}{2M}\nabla_R^2-\frac{1}{2}\left(1+\frac{1}{2M}\right)\nabla_r^2+V(\mathbf{r},\mathbf{R})+(1+\epsilon)F\hat{\boldsymbol{n}}\cdot\mathbf{r}, \tag{1}$$

where $\mathbf{R}$ is the vector joining the nuclei, $\mathbf{r}$ is the position vector of the electron measured from the midpoint of $\mathbf{R}, M$ is the mass of the proton or deuteron, $V(\mathbf{r},\mathbf{R})$ is the electrostatic interaction potential, and $(1+\epsilon)=1+(1+2M)^{-1}$. We use atomic units throughout. The change in energy of the system for small values of the applied field is given by $\Delta E=-\frac{1}{2}\alpha_d F^2$, where α_d is the polarizability. Thus if $\Psi^{(0)}(\mathbf{r},\mathbf{R})$ is the eigenfunction of the unperturbed system with Hamiltonian H_0 and E_0 is the eigenvalue, the polarizability can be written

$$\alpha_d=-2\langle\Psi^{(1)}|(1+\epsilon)\hat{\boldsymbol{n}}\cdot\mathbf{r}|\Psi^{(0)}\rangle, \tag{2}$$

where

$$(H_0-E_0)\Psi^{(1)}(\mathbf{r},\mathbf{R})+(1+\epsilon)\hat{\boldsymbol{n}}\cdot\mathbf{r}\Psi^{(0)}(\mathbf{r},\mathbf{R})=0. \tag{3}$$

Alternatively $\Psi^{(1)}$ can be determined from the stationary value of the functional

$$\mathcal{J}=\langle\Psi^{(1)}|H_0-E_0|\Psi^{(1)}\rangle+2(1+\epsilon)\langle\Psi^{(1)}|\hat{\boldsymbol{n}}\cdot\mathbf{r}|\Psi^{(0)}\rangle. \tag{4}$$

If we write $\Psi^{(1)}(\mathbf{r},\mathbf{R})$ as an expansion over some chosen basis set $\psi_n(\mathbf{r},\mathbf{R})$,

$$\Psi^{(1)}(\mathbf{r},\mathbf{R})=\sum_{n=1}^{N}Q_n\psi_n(\mathbf{r},\mathbf{R}), \tag{5}$$

assumed to diagonalize the unperturbed Hamiltonian H_0 so that $\langle\psi_n|H_0|\psi_{n'}\rangle=E_n\delta_{nn'}$, the polarizability may be written

$$\alpha_d=2(1+\epsilon)^2\sum_{n=1}^{N}\frac{|\langle\Psi^{(0)}|\hat{\boldsymbol{n}}\cdot\mathbf{r}|\psi_n\rangle|^2}{E_n-E_0}. \tag{6}$$

This expression for the polarizability is stationary with respect to first-order errors in $\Psi^{(1)}$ and is bounded from below.

The completeness of the set $\psi_n(\mathbf{r},\mathbf{R})$ can be assessed by inspecting other sum rules. Introduce the oscillator strength

$$f_n=2\left[(E_n-E_0)/\left(1+\frac{1}{2M}\right)\right]|\langle\Psi^{(0)}|\hat{\boldsymbol{n}}\cdot\mathbf{r}|\psi_n\rangle|^2 \tag{7}$$

and define the sum

$$S(p)=\sum_{n=1}^{\infty}\left[(E_n-E_0)\Big/\left(1+\frac{1}{2M}\right)\right]^p f_n, \tag{8}$$

so that

$$\alpha_d=(1+\epsilon)^2\left(1+\frac{1}{2M}\right)^{-1}S(-2). \tag{9}$$

Then, provided the ψ_n form a complete set,

$$S(-1)=\tfrac{2}{3}\langle\Psi^{(0)}|r^2|\Psi^{(0)}\rangle \tag{10}$$

and

$$S(0)=1. \tag{11}$$

1050-2947/99/60(4)/2630(3)/$15.00

TABLE I. Nonrelativistic evaluation of the sum $S(p)$, Eq. (8), for $H_2{}^+$ and $D_2{}^+$.

p	$H_2{}^+$	$D_2{}^+$
0	1.000 000 0(1)	1.000 000 0(2)
−1	1.653 650 96(2)	1.635 744 78(6)
−2	3.167 000 94(1)	3.071 152 0(2)
−3	6.780 745 959(7)	6.375 365 3(3)
−4	15.889 406 225(5)	14.325 799 4(6)

The eigenfunctions $\Psi^{(0)}(\mathbf{r},\mathbf{R})$ and $\psi_n(\mathbf{r},\mathbf{R})$ can be written as sums of products of nuclear and electronic wave functions of the form

$$\psi_s(\Lambda NM)=\left[\frac{2N+1}{4\pi}\right]^{1/2} D^{N*}_{M\Lambda}(\Theta,\Phi,0)\,\phi_{s\Lambda}(\mathbf{r},R)\,\chi_{s\Lambda}(R), \tag{12}$$

where (Θ,Φ) are angles specifying the orientation of the internuclear axis in the space-fixed frame, N is the total angular-momentum quantum number, M is the projection onto the space-fixed Z axis, Λ is the projection of the electronic angular momentum onto the internuclear axis, and $\mathbf{D}$ is the rotation matrix [6]. For the ground state of $H_2{}^+$ or $D_2{}^+$, $N=M=\Lambda=0$ and the electronic wave function has Σ_g^+ symmetry. The perturbed state is a superposition of states with $N=1, M=0$, and $\Lambda=0$ and ± 1, the electronic wave functions having Σ_u^+ and Π_u symmetry.

To calculate the matrix elements of the Hamiltonian and of the electric-dipole operator we transform from the space-fixed frame to the body-fixed frame following standard procedures [6,7]. The nuclear kinetic-energy operator may be written

$$-\frac{\nabla_R^2}{2M}=-\frac{1}{2MR^2}\frac{\partial}{\partial R}R^2\frac{\partial}{\partial R}+H_{\rm rot}, \tag{13}$$

where $H_{\rm rot}$ is given by

$$\begin{aligned} H_{\rm rot}&=\frac{1}{2MR^2}(\mathbf{N}-\mathbf{L})^2\\ &=\frac{1}{2MR^2}(N^2+L^2-N^-L^+-N^+L^--2\Lambda^2), \end{aligned} \tag{14}$$

in which $\mathbf{L}$ is the electronic angular momentum and ± indicates angular-momentum raising and lowering operators. These are the operators that couple Σ and Π states. The electronic wave functions for $H_2{}^+$ and $D_2{}^+$ are separable in prolate spheroidal coordinates and we expressed the electronic basis functions $\phi_{\alpha\Lambda}(\mathbf{r},R)$ in terms of these. The corresponding formulas for the matrix elements of $H_{\rm rot}$ are given by Moss and Sadler [8]. A detailed description of the representation of the nuclear and electronic eigenfunctions and the construction of the unperturbed eigenfunction $\Psi^{(0)}$ and the basis functions ψ_n together with a discussion of the convergence properties is given by Taylor *et al.* [9].

TABLE II. Comparison of theoretical nonadiabatic values of the electric-dipole polarizability for the ground states of $H_2{}^+$ and of $D_2{}^+$ with experimental values. The results from Refs. [1] and [4] have been multiplied by the factor $(1+\epsilon)^2$.

$H_2{}^+$	$D_2{}^+$	Ref.
$3.168\,0^{+0.0018}_{-0.0001}$	$3.067\,1^{+0.0016}_{-0.0020}$	[5], variational
3.168 2(4)	3.071 4(4)	[2], finite element
3.168 5	3.071 87	[4], artificial channel
3.168 3	3.071 78	[4], variational
3.168 725 6(1)	3.071 988 7(2)	This work
3.168 1(7)	3.071 2(7)	[1], experiment

The electric-dipole operator must also be transformed to the body-fixed axis. The necessary procedures are described by Lefebvre-Brion and Field [7]. For matrix elements of $\hat{\boldsymbol{n}}\cdot\mathbf{r}$ connecting Σ_g^+ states to Σ_u^+ states

$$\begin{aligned} &\langle N,\Lambda=0|\hat{\boldsymbol{n}}\cdot\mathbf{r}|N+1,\Lambda=0\rangle\\ &\quad=[(N+1)/3]^{1/2}\langle\Lambda=0|z|\Lambda=0\rangle \end{aligned} \tag{15}$$

and connecting Σ_g^+ states to Π_u states

$$\begin{aligned} &\langle N,\Lambda=0|\hat{\boldsymbol{n}}\cdot\mathbf{r}|N+1,\Lambda=\pm1\rangle\\ &\quad=\mp[(N+2)/3]^{1/2}\\ &\qquad\times\langle\Lambda=0|2^{-1/2}(x\mp iy)|\Lambda=\pm1\rangle, \end{aligned} \tag{16}$$

where $\mathbf{r}=(x,y,z)$. The calculation of $\langle 0|z|0\rangle$ and $\langle 0|x\mp iy|\pm1\rangle$ in prolate spheroidal coordinates is straightforward.

Calculations of $S(p)$ were carried out with basis sets ψ_n comprised of electronic and vibrational functions [9,10]. The converged values of $S(0)$ and $S(-1)$ obtained using 121 electronic and 11 vibrational basis functions are given in Table I. The convergence of the sum rules with basis-set size is approximately logarithmic. Errors were determined for each sum $S(p)$ by finding A and c such that Ae^{-cn} is the

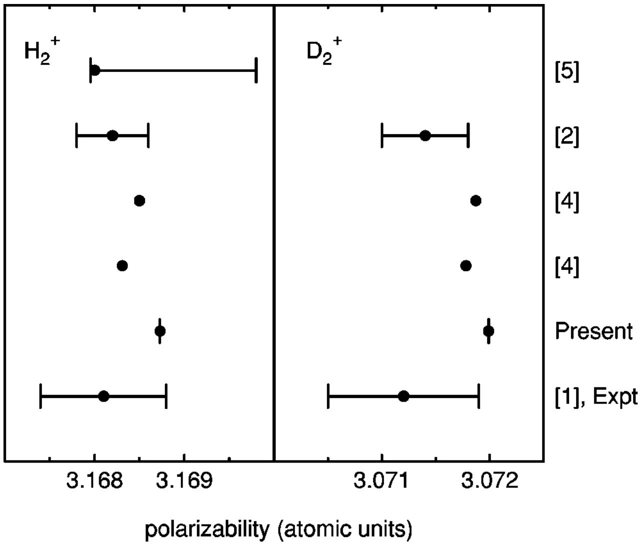

FIG. 1. Polarizabilities of $H_2{}^+$ and $D_2{}^+$ in their ground states. For each of the two calculations from the present work the error bar is within the vertical line crossing through the data point.

difference between the values obtained with basis sets of sizes $n\times n\times n$ and $(n+1)\times(n+1)\times(n+1)$. The total error given in Table I for each entry is $A\Sigma_{t=n}^{\infty}e^{-ct}=Ae^{-cn}[1-e^{-c}]^{-1}$.

The values of the calculated sums $S(0)$ and $S(-1)$ agree with the exact values [11,12] to better than 2 parts in 10^8. Table I also lists the values of $S(-2)$,$S(-3)$, and $S(-4)$. We anticipate no loss of accuracy in evaluating $S(-2)$, since the summation, Eq. (6), is stationary with respect to first-order errors. The corresponding values of the dipole polarizabilities α_d are given in Table II and Fig. 1. The sums $S(-3)$ and $S(-4)$ are related to quantities occurring in the determination of the polarizabilities [1,13–15]. $S(-3)$ enters in the combination $B_6\equiv\frac{3}{2}S(-3)-\frac{1}{10}C_0$, where C_0 is the scalar quadrupole polarizability. With $C_0=23.99$ for $H_2{}^+$ and 23.24 for $D_2{}^+$ [16], we predict that $B_6=7.77$ for $H_2{}^+$ and 7.24 for $D_2{}^+$. The empirical value for $H_2{}^+$ derived by Jacobson *et al.* [1] is 7.8(5).

Table II and Fig. 1 contain a comparison of our calculated values of α_d with experiment and with the results of other theoretical methods. We leave aside calculations of the polarizability corresponding to an electric field along the body-fixed axis [17,18]. Moss [4] employed a variational method and an artificial channel method, with a classical description of the rotation. We are able to reproduce his results with our procedure if we take $N=0$ for the intermediate states with the consequent neglect of Σ-Π coupling, the error introduced by ignoring rotational coupling being accordingly one in the fourth decimal place in the calculated polarizability. The calculations of Bhatia and Drachman [5] and Shertzer and Greene [2] make no approximations other than in the numerical applications of their methods and yield values consistent to within the precision they claim with our results.

We have determined the nonrelativistic electric-dipole polarizabilities of the lowest rotational state of $H_2{}^+$ and $D_2{}^+$ to a precision, we believe, of one part in 10^8. We expect that relativistic corrections will enter at the level of one part in 10^5 based on known corrections for the hydrogen atom [19]. Other effects arising from the finite size of the nucleus and nuclear spin will be still smaller. An analysis of the experimental data [1] incorporating our values of the sum rules may yield improved estimates of other properties that enter the interpretation.

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