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Nonadiabatic dipole polarizabilities of $H_2{}^+$ and $D_2{}^+$ ground states

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The recently reported discrepancy between the experimentally determined value for the dipole polarizabity of the $H_2{}^+$ ground state [Phys. Rev. A **56**, R4361 (1997); **57**, 4065 (1998)] and the adiabatic value calculated in the clamped nucleus approximation [Mol. Phys. **65**, 679 (1988)] has motivated a fully nonadiabatic treatment of the problem. Finite element analysis is used to obtain a direct solution of the zeroth- and first-order equations of perturbation theory. The nonadiabatic value for α_s is consistent with the experimental measurement. [S1050-2947(98)03108-4]

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I. INTRODUCTION

For a Rydberg state of a homonuclear diatomic molecule, the interaction between the excited electron and the molecular ion core can be described via an effective polarization potential which includes permanent and induced multipole moments of the core [1–3]. For a $J=0$ core, the lowest order terms in the polarization potential are $V=(B_4/r^4)+(B_6/r^6)+(B_7/r^7)+\cdots$, where B_4 is proportional to the scalar dipole polarizability. Microwave spectroscopy of high L Rydberg states has provided a mechanism for determining these moments experimentally [4–6]. Recently, Jacobson *et al.* reported an experimental value $\alpha_s=3.1681(7)e^2a_o^3$ for the ground-state scalar dipole polarizability of $H_2{}^+$ (using $B_4=-\alpha_s/2$) [7]. This is not in agreement with the adiabatic value calculated by Bishop and co-workers, who obtained $\alpha_s=3.1713e^2a_o^3$ in a clamped nucleus approximation [8–11]. It has been suggested [7] that the discrepancy is due to the neglected nonadiabatic effects in the calculation, and this study is an attempt to calculate those effects. In Sec. II, we outline our method for obtaining α_s nonadiabatically. In Sec. III, we compare our results with the adiabatic and experimental values.

II. METHOD

A. Transformation to the body-fixed frame

The three-body Hamiltonian for the homonuclear diatomic molecular ion $(m_1=m_2=m, m_3=1)$ in an external electric field $\vec{\mathcal{E}}=\mathcal{E}\hat{n}$ is given in atomic units as

$$\hat{H}=-\frac{\nabla_1^2}{2m}-\frac{\nabla_2^2}{2m}-\frac{\nabla_3^2}{2}+\frac{1}{|\vec{r}_1-\vec{r}_2|}-\frac{1}{|\vec{r}_1-\vec{r}_3|}-\frac{1}{|\vec{r}_2-\vec{r}_3|}-\mathcal{E}\hat{n}\cdot(\vec{r}_1+\vec{r}_2-\vec{r}_3). \tag{1}$$

The coordinates of the three particles with respect to the laboratory frame are $\mathbf{x}_1'$, $\mathbf{x}_2'$, and $\mathbf{x}_3'$, where the prime indicates the space-fixed (SF) frame. The direction of the electric field $\hat{n}$ must be specified in a SF frame. Defining

$$\vec{R}_{\rm cm}=\frac{m(\vec{r}_1+\vec{r}_2)+\vec{r}_3}{2m+1}, \tag{2a}$$

$$\vec{R}=\vec{r}_1-\vec{r}_2, \tag{2b}$$

$$\vec{r}=\vec{r}_3-\frac{\vec{r}_1+\vec{r}_2}{2}, \tag{2c}$$

we can separate out the center-of-mass (cm) motion. The Hamiltonian for the relative motion in the SF frame is

$$\hat{H}=-\frac{1}{2\mu}\nabla_R^2-\frac{1}{2}\nabla_r^2-\frac{1}{8\mu}\nabla_r^2+\frac{1}{R}-\frac{1}{\left|\frac{\vec{R}}{2}-\vec{r}\right|}-\frac{1}{\left|\frac{\vec{R}}{2}+\vec{r}\right|}+(1+\epsilon)\mathcal{E}\hat{n}\cdot\vec{r}, \tag{3}$$

where $\mu=m/2$ and $(1+\epsilon)=(2m+2)/(2m+1)$. The relative electronic and nuclear coordinates are represented as $\mathbf{x}'$ and $\mathbf{X}'$, respectively. For weak electric fields (one atomic unit is 5.142×10^9 V/cm), the last term can be treated using perturbation theory. The mass factor that scales the field-dependent term was discussed previously by Drachman [12]. The Hamiltonian $\hat{H}$, the total squared angular momentum $\hat{L}^2$, and the z' component of angular momentum $\hat{L}_{z'}$ are constants of motions with corresponding eigenvalues E, $L(L+1)$, and M.

We adopt the conventions introduced by Pack and Hirschfelder for diatomic molecular ions [13], whereby the transformation from the SF (primed) coordinates to the body-fixed (unprimed) coordinates is affected through a rotation $\mathcal{R}$ that aligns the z axis with $\vec{R}$, and leaves the y axis in the $x'y'$ plane. The matrix representation of $\mathcal{R}$ is $\mathbf{R}(\Phi',\Theta',0)$, where the Euler angles are the spherical polar coordinates of $\vec{R}$ in the SF frame. The electronic and nuclear coordinates in the body-fixed (BF) frame are related to those

1050-2947/98/58(2)/1082(5)/$15.00

in the SF frame by $\mathbf{x}=\mathbf{R}\mathbf{x}'$ and $\mathbf{X}=\mathbf{R}\mathbf{X}'$. The physical vectors $\vec{r}$ and $\vec{R}$ are unchanged in the frame transformation; only the *components* of vector are frame dependent. Since $\hat{L}^2$ and $\hat{H}$ are invariant with respect to rotation, they remain constants of the motion; $\hat{L}_z$ (with corresponding eigenvalue Ω) does *not* commute with $\hat{H}$ in the BF frame.

In the BF frame, the field-free Hamiltonian becomes

$$\hat{H}=\frac{\hat{p}_R^2}{2\mu}+\frac{\hat{L}_n^2}{2\mu R^2}-\frac{1}{2}\boldsymbol{\nabla}_r^2-\frac{1}{8\mu}\boldsymbol{\nabla}_r^2+V(\vec{r},R), \tag{4}$$

where

$$V(\vec{r},R)=\frac{1}{R}-\frac{1}{\sqrt{\dfrac{R^2}{4}+r^2-Rr\cos\theta}}-\frac{1}{\sqrt{\dfrac{R^2}{4}+r^2+Rr\cos\theta}}. \tag{5}$$

The BF Hamiltonian of Eq. (4) is identical to field-free SF Hamiltonian of Eq. (3) with one exception: $-\boldsymbol{\nabla}_R^2$ has been replaced with $\hat{p}_R^2+(\hat{L}_n^2/R^2)$, where $\hat{L}_n^2=\hat{L}^2+\hat{L}_e^2-2\hat{L}_z^2-\hat{L}_{e_-}\hat{L}_+-\hat{L}_{e_+}\hat{L}_-$. The transformation to the BF frame has eliminated two degrees of freedom, but the Hamiltonian is not diagonal in the basis spanned by the eigenstates of $\hat{L}$ and $\hat{L}_z$:

$$\hat{H}\Psi(L,\Omega)=H_{\Omega,\Omega}\Psi(L,\Omega)+H_{\Omega,\Omega+1}\Psi(L,\Omega+1)+H_{\Omega,\Omega-1}\Psi(L,\Omega-1), \tag{6a}$$

$$H_{\Omega,\Omega}=\frac{\hat{p}_R^2}{2\mu}+\frac{1}{2\mu R^2}[L(L+1)-2\Omega^2+\hat{L}_e^2]-\frac{1}{2}\boldsymbol{\nabla}_r^2-\frac{1}{8\mu}\boldsymbol{\nabla}_r^2+V(\vec{r},R), \tag{6b}$$

$$H_{\Omega,\Omega\pm1}=-\frac{\sqrt{L(L+1)-M(M\pm1)}}{2\mu R^2}\hat{L}_{e_\mp}. \tag{6c}$$

The SF wave function with total angular momentum L and z component M is related to the BF wave functions by

$$\Psi(\mathbf{x}',\mathbf{X}';L,M)=\sum_{\Omega=-L}^{L}\Psi(\mathbf{x},R;L,\Omega)\mathcal{D}_{\Omega M}^{L}(\mathcal{R}). \tag{7}$$

B. Perturbation theory

The scalar dipole polarizability α_s for a homonuclear diatomic molecular ion is defined in terms of the second-order correction to the energy $E^{(2)}$ induced by an external field fixed in the laboratory frame:

$$E^{(2)}=-\tfrac{1}{2}\alpha_s\mathcal{E}^2=\langle\Psi^{(1)}|(1+\epsilon)\mathcal{E}\hat{n}\cdot\vec{r}|\Psi^{(0)}\rangle. \tag{8}$$

$\Psi^{(0)}$ and $\Psi^{(1)}$ are solutions of the zeroth- and first-order equations of perturbation theory:

$$H\Psi^{(0)}=E^{(0)}\Psi^{(0)}, \tag{9a}$$

$$(H-E^{(0)})\Psi^{(1)}=-(1+\epsilon)\mathcal{E}\hat{n}\cdot\vec{r}\Psi^{(0)}. \tag{9b}$$

(The superscript in parentheses indicates the order of the perturbation.)

First we solve the zeroth-order equation for the ground-state energy $E^{(0)}$ and the corresponding wave function $\Psi^{(0)}$ *in the BF frame*. For the special case $L=0$, the BF Hamiltonian of Eq. (6) is diagonal:

$$\hat{H}\Psi^{(0)}(0,0)=\left[\frac{\hat{p}_R^2}{2\mu}+\left(\frac{1}{2}+\frac{1}{8\mu}\right)\hat{p}_r^2+\left(\frac{1}{2\mu R^2}+\frac{1}{2r^2}+\frac{1}{8\mu r^2}\right)\hat{L}_e^2+V(\vec{r},R)\right]\Psi^{(0)}(0,0). \tag{10}$$

The wave function $\Psi^{(0)}(\mathbf{x},R;0,0)$ is independent of the electronic azimuthal angle. Using the elliptical coordinates

$$R=R, \tag{11a}$$

$$\xi=\frac{r_1+r_2}{R}, \tag{11b}$$

$$\eta=\frac{r_1-r_2}{R}, \tag{11c}$$

where $r_{1,2}=\sqrt{R^2/4+r^2\pm rR\cos\theta}$, the eigenvalue problem described by Eq. (9a) is solved with three-dimensional finite element analysis as described in Ref. [14]. With this choice of coordinates, all the matrix elements are simple polynomials and can be evaluated exactly.

Next we solve the first-order equation of perturbation theory for the correction to the wave function $\Psi^{(1)}$ *in the BF frame*. If we choose the field along the laboratory z' axis, then

$$\hat{n}\cdot\vec{r}=\hat{z}'\cdot\vec{r}=\cos\Theta'\cos\theta-r\sin\Theta'\sin\theta\cos\phi \tag{12}$$

where Θ' is the Euler angle, and θ and ϕ are the electronic angular coordinates in the BF frame. The first-order correction to the wave function, which has $L=1,M_{z'}=0$ character owing to the Wigner-Eckart theorem, can be written as

$$\begin{aligned}\Psi^{(1)}(\mathbf{x}',\mathbf{X}';1,0)&=\sum_{\Omega=-1}^{1}\Psi^{(1)}(\mathbf{x},R;1,\Omega)\mathcal{D}_{\Omega1}^{1}(\mathcal{R})\\&=-\frac{\sin\Theta'}{\sqrt{2}}\Psi^{(1)}(\mathbf{x},R;1,-1)\\&\quad+\cos\Theta'\Psi^{(1)}(\mathbf{x},R;1,0)\\&\quad+\frac{\sin\Theta'}{\sqrt{2}}\Psi^{(1)}(\mathbf{x},R;1,1).\end{aligned} \tag{13}$$

Using Eqs. (12) and (13) in Eq. (9b), and noting that H and $\Psi^{(0)}$ are independent of the Euler angles, we can eliminate the dependence on Θ' by equating the terms proportional to $\sin\Theta'$ and $\cos\Theta'$, respectively:

$$(H_{0,0}-E^{(0)})\Psi^{(1)}(1,0)+H_{0,1}\Psi^{(1)}(1,1)+H_{0,-1}\Psi^{(1)}(1,-1) = -r\cos\theta\Psi^{(0)}(0,0), \tag{14a}$$

$$(H_{1,1}-E^{(0)})\frac{\Psi^{(1)}(1,1)}{\sqrt{2}}-(H_{-1,-1}-E^{(0)})\frac{\Psi^{(1)}(1,-1)}{\sqrt{2}} +(H_{1,0}+H_{-1,0})\Psi^{(1)}(1,0) = r\sin\theta\cos\phi\Psi^{(0)}(0,0), \tag{14b}$$

where

$$H_{0,0}=\frac{\hat{p}_R^2}{2\mu}+\frac{1}{\mu R^2}+\left(\frac{1}{2}+\frac{1}{8\mu}\right)\hat{p}_r^2 +\left(\frac{1}{2\mu R^2}+\frac{1}{2r^2}+\frac{1}{8\mu r^2}\right)\hat{L}_e^2+V(\vec{r},R), \tag{15a}$$

$$H_{1,1}=H_{-1,-1}=H_{0,0}-\frac{1}{\mu R^2}, \tag{15b}$$

$$H_{0,\pm 1}=H_{\mp 1,0}=-\frac{\hat{L}_{e_\mp}}{2\mu R^2}. \tag{15c}$$

We can now eliminate the ϕ dependence from Eq. (14) analytically. Since the right-hand side of Eq. (14a) is independent of ϕ, it follows that $\Psi^{(1)}(1,0)$ and $[\hat{L}_{e_-}\Psi^{(1)}(1,1)+\hat{L}_{e_+}\Psi^{(1)}(1,-1)]$ must be independent of ϕ. From Eq. (14b), we have the additional constraint that $[\Psi^{(1)}(1,1)-\Psi^{(1)}(1,-1)]$ must be proportional to $\cos\phi$. It is straightfoward to show that these equations are satsified *only* if

$$\Psi^{(1)}(1,0)=f(r,\theta,R), \tag{16a}$$

$$\Psi^{(1)}(1,\pm 1)=\pm\frac{1}{\sqrt{2}}g(r,\theta,R)\exp(\pm i\phi), \tag{16b}$$

where f and g are still undetermined functions of the remaining three variables. Substituting Eq. (16) into Eq. (14), we obtain a set of coupled equations for the functions f and g:

$$(H_{0,0}-E^{(0)})f+\frac{1}{\mu R^2}\left(\frac{\partial}{\partial\theta}+\cot\theta\right)g=-r\cos\theta\Psi^{(0)}, \tag{17a}$$

$$\left[H_{1,1}-E^{(0)}+\left(\frac{1}{2\mu R^2}+\frac{1}{2r^2}+\frac{1}{8\mu r^2}\right)\frac{1}{\sin^2\theta}\right]g+\frac{1}{\mu R^2}\frac{\partial}{\partial\theta}f = r\sin\theta\Psi^{(0)}, \tag{17b}$$

where $f(r,\pi-\theta,R)=-f(r,\theta,R)$ and $g(r,\pi-\theta,R)=g(r,\theta,R)$. The symmetry conditions on f and g, along with Eqs. (13) and (16), guarantee that the wave function $\Psi^{(1)}$ has odd total parity. Because of the indicial behavior of $g(r,\theta,R)$ at $\theta=0$, we also require that g vanish at $\theta=0$. Carrying out a transformation to elliptical coordinates ξ, η, and R, we solve the resulting set of linear equations using three-dimensional (3D) finite element (FE) analysis subject to the appropriate boundary conditions. Because the function $g(\xi,\eta,R)$ goes to zero very rapidly at $\xi=1$ and $\eta=\pm 1$, a much finer mesh is needed in the vicinity of these points in order to obtain an accurate representation of the wave function. Unlike the solution of the zeroth-order equation, the matrix elements arising from $\hat{L}_e^2$ and $\hat{L}_{e\pm}$ operating on $\cos\phi$ are not simple polynomials in elliptical coordinates and must be integrated numerically. The zeroth-order wave function and first-order wave functions, which are represented as products of FE basis functions and analytical functions of Θ',Φ' and ϕ, can now be used in Eq. (8) to obtain the polarizability.

III. RESULTS

The zeroth- and first-order equations of perturbation theory were solved for $H_2{}^+$ and $D_2{}^+$ using identical FE grids. The results reported were obtained using 360 elements; the 3D space was truncated and discretized as follows:

R:	0	0.8	1.4	1.8	2	2.2	2.6	3.2	4	6	10
ξ:	1	1.001	1.1	1.5	2	2.5	3	4	6	12	
η:	0	0.5	0.9	0.999	1					.	

The local basis functions were products of fourth degree polynomials in three variables; over 23 000 basis functions were used to approximate each of the three functions $\Psi^{(0)},f$, and g.

The FE ground-state energy for $H_2{}^+$ is $-0.597\,139\,055\,(8)$ a.u., where the number in parentheses is the error in the last digit. The error was determined by comparison with the best variational result of $-0.597\,139\,063\,123$ a.u. [15,16]. For $D_2{}^+$, the FE energy is $-0.598\,787\,6(11)$, compared to the variational value $-0.598\,788\,784\,331$ [17,18]. The slower convergence for $D_2{}^+$ as compared to $H_2{}^+$ is a consequence of the increased localization of the wave function about the equilibrium separation. The energy was very stable with respect to variations in the grid. The small elements near $\eta=1$ and $\xi=1$ could be completely eliminated without any loss of accuracy to the energy.

Our intent here was not to obtain benchmark values for the ground-state energy; rather we attempted to find a ‘‘universal’’ grid on which the equations of perturbation theory for both systems could be solved with sufficient accuracy to

TABLE I. The nonadiabatic values for the scalar polarizability of $H_2{}^+$ and $D_2{}^+$ are compared with experimental calculations and two adiabatic calculations: the clamped nucleus approach and the sum over rovibronic states method. Experimental results *include* the factor of $(1+\epsilon)^2$ as explained in the text. The clamped nucleus calculation does not include $(1+\epsilon)$ in the perturbation. All results are in atomic units.

System	Method	α_s
$H_2{}^+$	Clamped nucleus [a]	3.1713
	Adiabatic [b]	3.1667
	Experiment [c]	3.1681(7)
	FE nonadiabatic [d]	3.1682(4)
$D_2{}^+$	Clamped nucleus [a]	3.0731
	Adiabatic [b]	3.0708
	Experiment [c]	3.0712(7)
	FE nonadiabatic FE [d]	3.0714(4)

[a] Bishop and Lam [10].

[b] Clark and Greene [22].

[c] Jacobson *et al.* [7].

[d] Babb [21].

determine the nonadiabatic contributions to the polarizabilty. Ground-state energies obtained with the adaptive FE method, which automatically refines the grid for energy optimization, are far more accurate: $-0.597\,139\,062(1)$ for $H_2{}^+$ and $-0.598\,788\,779(5)$ for $D_2{}^+$ [19,20].

The accuracy of the FE wave function $\Psi^{(0)}$ can be estimated from the error in expectation values of non-Hamiltonian operators. In Ref. [14], the error for $H_2{}^+$ FE expectation values is only one order of magnitude greater than the error in the FE energy, even for the delta function operator $\langle \delta(r_1) \rangle$. We therefore assume that the error in wave function for $H_2{}^+(D_2{}^+)$ is on the order of $10^{-7}(10^{-5})$. This is considerably higher than one expects based on the error in the energy, and is a direct consequence of local interpolation. We conclude that the error in $\Psi^{(0)}$ is not a significant source of uncertainty in the final value for the polarizability for $H_2{}^+$. For $D_2{}^+$, any overestimation of the polarizability due to the error in the binding energy of the ground state is well within the final error bars. (A smaller binding energy implies larger polarizability, since the state is more easily distorted in the field.)

The sensitivity of the polarization to the grid discretization, particularly near $\eta=1$ and $\xi=1$, and the residual error from numerical integration of certain matrix elements, were the main sources of the stated uncertainty of ± 0.0004 in the final values for α_s. This is believed to be a fair estimate of the final error based on convergence studies in which the number of Gauss quadrature points and the element size near $\eta=1$ and $\xi=1$ were varied.

In Table I, the FE nonadiabatic values for the polarizability of the ground state are compared with experiment and two adiabatic calculations: the clamped nucleus calculation of Bishop and co-workers [8–10] and a recent calculation by Clark and Greene [22] which uses a sum over rovibronic states. Various approaches for obtaining the polarizability in the adiabatic approximation were discussed in Ref. [11].

In the clamped nucleus approximation, the electronic motion is perturbed by the electric field, and the polarizability is obtained as a function of the internuclear separation:

$$-\frac{1}{2}\alpha(R)\mathcal{E}^2=\sum_n \frac{|\langle \psi_n(R;\vec{r})|\vec{\mathcal{E}}\cdot\vec{r}|\psi_0(R;\vec{r})\rangle|^2}{E_0(R)-E_n(R)}. \tag{18}$$

Here $E_n(R)$ and $\psi_n(R;\vec{r})$ are the BO electronic potential energy and wave function at fixed R. [The results of Bishop and co-workers do not include the factor of $(1+\epsilon)$ in the perturbation; this is consistent with perturbing only the electronic state.] $\alpha(R)$ is then averaged over the rovibronic state $f_{J,v}(\vec{R})$. For the ground-state polarizability, we have

$$\alpha_s=\langle f_{0,0}(\vec{R})|\alpha(R)|f_{0,0}(\vec{R})\rangle. \tag{19}$$

In the sum over rovibronic states approach, the adiabatic molecular wave function is written as a product of an electronic and nuclear function. The molecule *as a whole* is perturbed by the field:

$$-\frac{1}{2}\alpha\mathcal{E}^2 =\sum_{n,J,v} \frac{|\langle \psi_n(R\vec{r})f_{J,v}(\vec{R})|(1+\epsilon)\vec{\mathcal{E}}\cdot\vec{r}|\psi_0(R;\vec{r})f_{0,0}(\vec{R})\rangle|^2}{E_{0,0,0}-E_{n,J,v}}. \tag{20}$$

This approach is expected to be an improvement over the clamped nuclear approximation, as it includes the effect of the perturbation on the nuclear motion.

The experimental results from Ref. [7] have been multiplied by $(1+\epsilon)^2$ to be consistent with our definition of α_s, which includes the factor $(1+\epsilon)$ from the center-of-mass separation as part of the perturbation. In Eq. (5) of Ref. [7], the coefficient of the quadrupole term is given as $B_4=-(1+\epsilon)^2(\alpha_s/2)$; we have instead taken $B_4=-\alpha_s/2$. It is the value of B_4 that is fitted to the experimental data. The nonadiabatic results agree with experiment within the stated uncertainties. The difference between the nonadiabatic and the clamped nucleus results for $H_2{}^+$ is double that for $D_2{}^+$ as expected.

In conclusion, nonadiabatic theory and experiment are in agreement at the current level of accuracy. Finally, we note that several other groups are in the process of calculating the nonadiabatic dipole polarizability of $H_2{}^+$ and $D_2{}^+$. Preliminary results from Moss, who obtained rotationally averaged polarizabilities from scattering theory, are in good agreement with the FE results [23]. Bhatia and Drachman have also calculated the polarizabilities using second-order perturbation theory with intermediate *p* pseudostates [24].

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