

Simple Approximate Eigenfunctions for an Electron in a Finite Dipole Field*

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Ground-state energy eigenvalues for an electron in a stationary finite electric-dipole field are calculated by a novel variational approach. The physical model is taken to be a perturbed hydrogen atom. Accurate energy eigenvalues are obtained for a large range of dipole moments. The simple variational functions used compare favorably with more nearly exact eigenfunctions obtained in complex calculations.

I. INTRODUCTION

Extensive variational calculations have recently been made to obtain ground-state energy eigenvalues and eigenfunctions for an electron moving in the field of a stationary finite electric dipole.¹ Among the physical problems to which this model has been applied are low-energy electron scattering by polar molecules and ion pairs in semiconductors and binding in color centers.²

In Ref. 1, the finite dipole was considered to be a two-center system and the variational functions were written in elliptic-hyperbolic coordinates. Extremely accurate eigenvalues and eigenfunctions were obtained for values of dipole moment D from $0.6393ea_0$ (e = electronic charge and a_0 = radius of first Bohr orbit in hydrogen), the minimum value required for binding, to $400ea_0$. Subsequently, these eigenfunctions were transformed to spherical polar coordinates by numerical integration.³ This partial-wave analysis was made for two systems, one with origin at the positive dipole charge, and the other with origin at the dipole center.

In the present work, the electron-dipole system is represented as a hydrogen atom perturbed by a distant negative charge. This is essentially a one-center viewpoint with the positive charge of the atom taken as the center. In the following sections, the form of the variational wave function is derived, the expectation value of the Hamiltonian is calculated and minimized with respect to the variational parameter, and energy eigenvalues are obtained. The energy eigenvalues and eigenfunctions obtained here are compared with the results of Refs. 1 and 3.

II. VARIATIONAL WAVE FUNCTION

The geometry of the physical system is shown⁴ in Fig. 1. The positive charge q is fixed at the origin of coordinates. The electron of charge $-e$ is at a distance r from the origin and makes an angle θ with the positive z axis. A charge $-q$ is located on the negative z axis at a distance R from the

origin. The distance from $-q$ to $-e$ is r' . The two fixed charges $\pm q$ comprise a stationary finite dipole of moment $D = qR$.

The Hamiltonian for the electron in the dipole field is

$$H = -\frac{1}{2}\nabla^2 - q/r + q/r' \quad (1)$$

in atomic units. The unperturbed problem is considered to be that of a hydrogenlike atom with Hamiltonian

$$H_0 = -\frac{1}{2}\nabla^2 - q/r. \quad (2)$$

The perturbation is

$$h = q/r' = q(r^2 + R^2 + 2rR \cos\theta)^{-1/2}. \quad (3)$$

The form of the variational wave function to be used in the following sections will be derived here by means of perturbation theory.⁵

For $q = 1$, H_0 becomes the Hamiltonian of the hydrogen atom⁶ (and the dipole moment D becomes numerically equal to the charge separation R). The ground-state energy eigenfunction is⁷

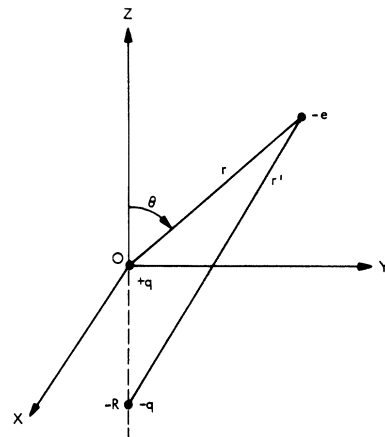


FIG. 1. Geometry for an electron in a stationary finite electric-dipole field.

$$\phi_g = \pi^{-1/2} e^{-r}. \quad (4)$$

The first-order correction to ϕ_g is, by standard perturbation theory,^{7,8}

$$\phi'_g = r(\frac{1}{2}r + 1)R^{-2} \cos\theta \phi_g. \quad (5)$$

The variational wave function is then taken to be simply a linear combination of ϕ_g and ϕ'_g ;

$$\psi \equiv n e^{-r} [1 + ar(\frac{1}{2}r + 1)R^{-2} \cos\theta], \quad (6)$$

where a is the linear variational parameter and n is the normalization constant readily calculated to be

$$n = \pi^{-1/2} \left(1 + \frac{43a^2}{8R^4}\right)^{-1/2}. \quad (7)$$

(n has been taken real and positive without loss of generality.)

III. VARIATIONAL CALCULATION

The basic approach in this section is to calculate the expectation value $\langle H \rangle$ of the Hamiltonian in Eq. (1), using the variational wave function ψ in Eq. (6), and then to minimize $\langle H \rangle$ with respect to the variational parameter a . Most of the calculation of $\langle H \rangle$ is simply a matter of straightforward, but lengthy, differentiation and/or integration. The result is

$$\begin{aligned} \langle H \rangle = & \left(1 + \frac{43a^2}{8R^4}\right)^{-1} \left(-\frac{1}{2} - \frac{7a^2}{16R^4} - f_0(R) - \frac{8a}{3R^2} f_1(R) \right. \\ & \left. + \frac{4a^2}{15R^4} f_2(R) \right), \end{aligned}$$

where

$$\begin{aligned} f_0(R) &= e^{-2R}(1 + R^{-1}) - R^{-1}, \\ f_1(R) &= -\frac{3}{8}e^{-2R}(R^2 + 5R + 9 + 9R^{-1} + \frac{9}{2}R^{-2}) + \frac{27}{16}R^{-2}, \end{aligned} \quad (8)$$

and

$$\begin{aligned} f_2(R) &= -\frac{15}{32}e^{-2R}(2R^4 + 18R^3 + 72R^2 + 180R + 325 \\ &+ 427R^{-1} + 384R^{-2} + 192R^{-3}) + \frac{645}{32}R^{-1} + 90R^{-3}. \end{aligned}$$

The condition for the extrema of $\langle H \rangle$ is

$$\frac{\partial}{\partial a} \langle H \rangle = 0, \quad (9)$$

which results in the following algebraic equation for a :

$$c_2 a^2 + c_1 a + c_0 = 0,$$

where

$$\begin{aligned} c_2 &= -\frac{43}{3}R^{-6}f_1(R), \\ c_1 &= -R^{-4} \left[\frac{9}{2} + \frac{43}{4}f_0(R) + \frac{8}{15}f_2(R) \right], \end{aligned} \quad (10)$$

and

$$c_0 = \frac{8}{3}R^{-2}f_1(R).$$

The coefficient of the cubic term, which in principle is present in Eq. (9), vanishes. The solution of

Eq. (10) is easily done and the numerical results are presented in Sec. IV.

IV. NUMERICAL RESULTS

Equation (10) has been solved for a large range of values of R corresponding to dipole moments D . [In every case, the minimum for $\langle H \rangle$ is yielded by the larger (positive) value of a .] The value of the linear variational parameter a which minimizes $\langle H \rangle$ has been labeled a' , and the corresponding value of $\langle H \rangle$ is $\langle H' \rangle$. The results are summarized in Table I, along with energies from the earlier work of Turner, Anderson, and Fox¹ for comparison.

The agreement between the variational energies calculated here and in Ref. 1 is surprisingly good. For most of the range of dipole moments, the discrepancy is less than 1%. However, when the critical dipole moment^{9,10} $D_{\text{crit}} = 0.6393ea_0$ is approached, the present simplified calculation gives increasingly poor results, eventually producing positive values of $\langle H' \rangle$. The more extensive calculations of Ref. 1 are clearly essential for dipole moments near the critical value.

It is interesting to compare the wave functions ψ' (corresponding to a') calculated here with those in Ref. 1. Those wave functions, originally calculated in elliptic-hyperbolic coordinates, have been

TABLE I. Variational parameter a' [Eq. (6)] and energy $\langle H' \rangle$ [Eq. (8)] for a range of dipole moment D .

$D(ea_0)^a$	a'	$-\langle H' \rangle (e^2/2a_0)^b$	
		This work	Turner <i>et al.</i> ^c
100	0.999 989	0.980 000	0.980 000
50	0.999 914	0.960 000	0.960 000
40	0.999 831	0.950 002	0.950 003
30	0.999 598	0.933 338	0.933 338
25	0.999 304	0.920 012	0.920 013
20	0.998 635	0.900 028	0.900 028
15	0.996 744	0.866 756	0.866 756
10	0.988 924	0.800 446	0.800 456
9	0.984 787	0.778 454	0.778 474
8	0.978 325	0.751 074	0.751 113
7	0.967 678	0.716 100	0.716 179
6	0.949 050	0.669 964	0.670 150
5	0.914 655	0.606 594	0.607 096
4	0.849 788	0.514 930	0.516 588
3	0.732 141	0.373 258	0.380 303
2	0.540 746	0.136 155	0.176 264
1.647 57	0.455 402	0.014 991	0.094 309
1.188 00	0.334 882	-0.182 526	0.014 171
1.000 02	0.284 605	-0.275 668	0.002 049

^aIn the present work, the dipole moment D is numerically equal to the dipole charge separation R , since $D(\text{in } ea_0) = q(=1, \text{ in } e) R(\text{in } a_0)$.

^bAlthough atomic units are used throughout the present work and e^2/a_0 is the energy unit, $\langle H' \rangle$ is given here in rydbergs ($1 \text{ Ry} = e^2/2a_0$) for ease in comparison with the already published results of Ref. 1.

^cReference 1.

transformed to spherical polar coordinates^{3,11} which are more convenient for the present purpose. The following integral has been evaluated numerically^{4,12} for the range of values of D in Table I:

$$X \equiv 2\pi \int_0^\infty r^2 dr \int_0^\pi \sin\theta d\theta |\psi' - \psi_{(\text{Ref. 3})}|^2. \quad (11)$$

For $D \geq 15$, one obtains $X < 10^{-6}$; for $D = 10, 5, 3, 2$, and 1 , $X = 2.5 \times 10^{-6}, 2.0 \times 10^{-4}, 6.9 \times 10^{-3}, 7.2 \times 10^{-2}$, and 1.4 , respectively. It may be inferred from this that the variational wave function ψ' is close to the more accurate ψ of Refs. 1 and 3, until the lower range of dipole moments is reached.

V. CONCLUDING REMARKS

The model of a hydrogen atom perturbed by a distant negative charge has been considered as a characterization of an electron in a stationary finite electric-dipole field. A variational function, whose form was derived from a second-order perturbation calculation, was used to calculate energies of the model for a large range of dipole moments. The resulting energies and wave functions compare favorably with those of more extensive calculations^{1,3,11} for $D \geq 3ea_0$. This region of validity of the present calculations may be understood on a simple physical basis. The requirement that the perturbing negative charge be well outside the hy-

drogenlike atom is $R \gg a_0/q$, or $qR \equiv D \gg 1$, in a.u. This criterion is in good accord with the present results.

The variational wave function determined here has an angular dependence which is S plus P wave. The linear variational parameter reflects the amount of mixing of S and P . An estimate of this mixing is given by a'/R^2 [see Eq. (6) and Table I], which is $10^{-4}, 10^{-2}$, and 8×10^{-2} for D of 100, 10, and $3ea_0$, respectively.

Finally, it should be noted that the variational function which first gave an accurate estimate of the critical dipole moment required for binding¹³ also has S - plus P -wave character. In that case, there were two nonlinear variational parameters; furthermore, the S and P waves had the same radial dependence.

The form of the wave function determined in the present work may be useful in further calculations, including those in which the finite dipole is free to rotate.¹⁴

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¹J. E. Turner, V. E. Anderson, and K. Fox, Phys. Rev. **174**, 81 (1968).

²See Ref. 1 for a comprehensive bibliography.

³W. R. Garrett, J. E. Turner, and V. E. Anderson, Phys. Rev. **188**, 513 (1969).

⁴The notation here is slightly different from that used in Refs. 1 and 3. The correspondence is

$$(r, \theta, r')_{(\text{this work})} = (r_1, \theta_1, r_2)_{(\text{Ref. 3})},$$

$$\text{origin (this work)} = \text{origin (Ref. 3)} + R/2.$$

⁵It should be emphasized that the variational calculation to follow will have advantages over a perturbation calculation in two important ways. First, the exact potential will be used, so that there will be no question about the error made in truncating an expansion of the

potential. Second, the question of the convergence of a perturbation series will be eliminated.

⁶For $q \neq 1$, a variational wave function depending on e^{-qr} would be derived. Calculations with such functions have already been made (see Ref. 13 below). However, the intention of the present work is to use only a *linear* variational parameter; it will be seen that this leads to surprisingly accurate results.

⁷For example, see L. I. Schiff, *Quantum Mechanics* (McGraw-Hill, New York, 1955), p. 80.

⁸For example, see A. Dalgarno, in *Quantum Theory I. Elements*, edited by D. R. Bates (Academic, New York, 1961), p. 172.

⁹J. E. Turner and K. Fox, Phys. Letters **23**, 547 (1966).

¹⁰M. H. Mittleman and V. P. Myerscough, Phys. Letters **23**, 545 (1966).

¹¹W. R. Garrett, J. E. Turner, and V. E. Anderson, Oak Ridge National Laboratory Report No. ORNL-4431, 1969 (unpublished).

¹²In the actual numerical integration of Eq. (11), the upper limit on the radial integral is the finite value of r for which $\psi^2_{(\text{Ref. 3})} \approx 0$.

¹³K. Fox and J. E. Turner, J. Chem. Phys. **45**, 1142 (1966).

¹⁴For example, see W. R. Garrett, Chem. Phys. Letters **5**, 393 (1970).