The Polarizability of H^-

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The value for the polarizability of H^- is computed from both third and sixth order Hylleraas type wave functions. It is found to be 11.58×10^{-24} and 14.63×10^{-24}, respectively, in c.g.s. units.

THE polarizabilities of helium and ionized lithium in an electric field have been computed by Hassé[1] and Baber using the variation method with unperturbed wave functions of the Hylleraas[2] type. Essentially the same method is applied here to compute the polarizability of H^-

The equation in which we must make the energy a minimum is

$$E\int\psi^2d\tau=\int\sum_i(\mathrm{grad}_i\,\psi)^2d\tau+2\int V\psi^2d\tau. \quad (1)$$

In this equation

$$E=E_0+\epsilon;\quad \psi=\psi_0(1+\varphi);\quad V=V_0+V'; \quad (2)$$

where

$$V_0=-Z/r_1-Z/r_2+1/r_{12};\qquad V'=-F(x_1+x_2). \quad (3)$$

The quantities are in terms of atomic units, with the energy unit being the ionization energy of hydrogen from the ground state. The distances of the two electrons from the nucleus are r_1 and r_2, respectively; x_1 and x_2, etc., refer to the Cartesian coordinates of the respective electrons measured from the nucleus, and r_{12} is the separation of the two electrons. E_0 is the energy of the unperturbed ground state; ϵ is the change in energy due to the presence of the field, F. ψ_0 is the unperturbed wave function for the ground state and $(1+\varphi)$ represents the factor by which the unperturbed wave function is to be multiplied in order to obtain the perturbed wave function. The function φ is assumed to be of the form

$$\varphi=A(x_1+x_2)+B(x_1r_1+x_2r_2). \quad (4)$$

Introducing Eq. (2) in Eq. (1) we have

$$\begin{aligned}E\int\psi_0^2(1+\varphi)^2d\tau&=\int(1+\varphi)^2\sum_i(\mathrm{grad}_i\,\psi_0)^2d\tau\\&+\int\psi_0^2\sum_i(\mathrm{grad}_i\,\varphi)^2d\tau\\&+2\int(1+\varphi)\psi_0\sum_i(\mathrm{grad}_i\,\varphi\cdot\mathrm{grad}_i\,\psi_0)d\tau\\&+2\int V_0\psi_0^2(1+\varphi)^2d\tau+2\int V'\psi_0^2(1+\varphi)^2d\tau. \quad (5)\end{aligned}$$

In solving for the unperturbed wave function the solution was made with the condition that

$$E_0\int\psi_0^2d\tau=\int\sum_i(\mathrm{grad}_i\,\psi_0)^2d\tau+2\int V_0\psi_0^2d\tau. \quad (6)$$

In addition we find by integrating by parts that

$$\int\varphi^n\sum_i(\mathrm{grad}_i\,\psi_0)^2d\tau+\int\psi_0\sum_i(\mathrm{grad}_i\,\psi_0\cdot\mathrm{grad}_i\,\varphi^n)d\tau=-\int\psi_0\varphi^n\sum_i\Delta_i\psi_0d\tau. \quad (7)$$

Now introducing Eqs. (6) and (7) into Eq. (5) we find that

$$\begin{aligned}\epsilon\int(1+2\varphi+\varphi^2)\psi_0^2d\tau&=-\int\psi_0(2\varphi+\varphi^2)\\&\times[\textstyle\sum_i\Delta_i\psi_0+(E-2V_0)\psi_0]d\tau\\&+\int\psi_0^2\sum_i(\mathrm{grad}_i\,\varphi)^2d\tau\\&+2\int V'\psi_0^2(1+2\varphi+\varphi^2)d\tau. \quad (8)\end{aligned}$$

Now ψ_0 is not an exact solution of the unperturbed wave equation. However, with a third- or

[1] H. R. Hassé, Proc. Camb. Phil. Soc. **26**, 542 (1930); **27**, 66 (1931); T. D. H. Baber and H. R. Hassé, Proc. Camb. Phil. Soc. **33**, 253 (1937).
[2] E. A. Hylleraas, Zeits. f. Physik **54**, 347 (1929).

TABLE I. Constants and polarizabilities.

Units	Order	He α	He A/F	He B/F	H^- α	H^- A/F	H^- B/F
Atomic	3rd	2.62	0.2859	0.3657	156.3	1.679	1.151
Atomic	6th	2.72	0.2888	0.3727	197.5	1.418	1.340
c.g.s.	3rd	0.1942×10^{-24}	—	—	11.58×10^{-24}	—	—
c.g.s.	6th	0.2016×10^{-24}	—	—	14.63×10^{-24}	—	—

sixth-order Hylleraas type wave function, the error will probably not be large if we set the first integral on the right-hand side in Eq. (8) equal to zero.

In addition the Hylleraas type wave function is expressible as $\psi_0(r_1, r_2, r_{12})$. Consequently, in terms of Cartesian coordinates we have

$$\psi_0(x_1, x_2, \cdots, z_2)=\psi_0(-x_1, -x_2, \cdots, -z_2). \quad (9)$$

The functions φ and V' contain factors of x_1 or x_2 so that we may expect certain integrals to vanish in the present case. In particular,

$$\int \varphi\psi_0^2 d\tau=0; \quad \int V'\psi_0^2 d\tau=0; \quad \int V'\psi_0^2\varphi^2 d\tau=0. \quad (10)$$

Also, for small values of the field strength F we may neglect the term $\epsilon\int\varphi^2\psi_0^2 d\tau$.

Consequently, Eq. (8) becomes

$$\epsilon\int\psi_0^2 d\tau=\int\psi_0^2\sum_i(\text{grad}_i\,\varphi)^2 d\tau+4\int V'\varphi\psi_0^2 d\tau. \quad (11)$$

On performing the differentiations, etc., we find that

$$\sum_i(\text{grad}_i\,\varphi)^2 d\tau=2A^2+2AB\left(r_1+r_2+\frac{x_1^2}{r_1}+\frac{x_2^2}{r_2}\right)+B^2\{r_1^2+r_2^2+3(x_1^2+x_2^2)\}, \quad (12)$$

and

$$-V'\varphi=AF(x_1^2+2x_1x_2+x_2^2)+BF\{x_1^2r_1+x_1x_2(r_1+r_2)+x_2^2r_2\}. \quad (13)$$

Then it is found convenient first to express the integrands in terms of the variables (r_1, r_2, r_{12}). Since the unperturbed function ψ_0 is a function only of these variables, we see from symmetry that

$$\int x_1^{2n}\psi_0^2 d\tau=\tfrac{1}{3}\int(x_1^{2n}+y_1^{2n}+z_1^{2n})\psi_0^2 d\tau, \quad (14)$$

and

$$\int x_1x_2\psi_0^2 d\tau=\tfrac{1}{3}\int(x_1x_2+y_1y_2+z_1z_2)\psi_0^2 d\tau. \quad (15)$$

Hence, we find

$$\int\psi_0^2\sum_i(\text{grad}_i\,\varphi)^2 d\tau=\int\psi_0^2(\text{grad}\,f)^2 d\tau, \quad (16)$$

where

$$(\text{grad}\,f)^2=2A^2+\tfrac{8}{3}AB(r_1+r_2)+2B^2(r_1^2+r_2^2). \quad (17)$$

Also, we find

$$4\int V'\varphi\psi_0^2 d\tau=4\int P\psi_0^2 d\tau, \quad (18)$$

where

$$-P=\frac{AF}{3}\{2(r_1^2+r_2^2)-r_{12}^2\}+\frac{BF}{3}\{r_1^3+r_2^3+\tfrac{1}{2}(r_1+r_2)(r_1^2+r_2^2-r_{12}^2)\}. \quad (19)$$

We now introduce the Hylleraas variables; i.e., we let

$$s=r_1+r_2; \quad t=r_2-r_1; \quad u=r_{12}. \quad (20)$$

Using these we have

$$(\text{grad}\,f)^2=2A^2+\tfrac{8}{3}ABs+B^2(s^2+t^2), \quad (21)$$

and

$$-4P=\tfrac{4}{3}AF(s^2+t^2-u^2)+\tfrac{2}{3}BF(s^3+2st^2-su^2). \quad (22)$$

The Hylleraas type wave function used is

$$\psi_0 = e^{-ns}(1+cu+dt^2+es+fs^2+gu^2). \quad (23)$$

We see that all of the functions that we need to integrate are symmetrical in r_1 and r_2—or involve only even powers of t—so that, if the general integrand is $g(r_1, r_2, r_{12})$, we have

$$\int g(r_1, r_2, r_{12})d\tau = 2\pi^2 \int_0^\infty ds \int_0^s du \times \int_0^u G(s, t, u)u(s^2-t^2)dt. \quad (24)$$

These can all be broken down into terms of the following type $\int\int\int e^{-2ns}s^a t^b u^c dsdtdu$, where

$$\int\int\int e^{-2ns}s^a t^b u^c dsdtdu = \frac{1}{(2n)^{3+a+b+c}}\left[\frac{(a+b+c+2)!}{(b+1)(b+c+2)}\right] = \frac{1}{(2n)^{3+a+b+c}}[a, b, c]. \quad (25)$$

Then, if we express the volume factor separately, we have

$$2\pi^2\int\int\int e^{-2ns}s^a t^b u^c \cdot u(s^2-t^2)dsdtdu = \frac{2\pi^2}{(2n)^{6+a+b+c}}\{a, b, c\}, \quad (26)$$

where

$$\{a, b, c\} = [a+2, b, c+1]-[a, b+2, c+1]. \quad (27)$$

We now introduce the following substitution

$$C_{ijk} = \int s^i t^j u^k \psi_0^2 d\tau, \quad (28)$$

whence Eq. (11) may be written as

$$C_{000\epsilon} = 2A^2C_{000} + \tfrac{8}{3}ABC_{100} + B^2(C_{200}+C_{020}) - \tfrac{4}{3}AF(C_{200}+C_{020}-C_{002}) - \tfrac{2}{3}BF(C_{300}+2C_{120}-C_{102}). \quad (29)$$

Applying the Ritz method we must minimize the ϵ with respect to A and B (i.e., $\partial\epsilon/\partial A=0$, $\partial\epsilon/\partial B=0$). The solution of the resulting two equations gives the values of A and B in terms of F—and so gives the perturbed wave function.

If α represents the polarizability of the system, we have

$$\epsilon = -\tfrac{1}{2}\alpha F^2. \quad (30)$$

To convert α to c.g.s. units from the atomic units used it is necessary to multiply by $0.7410 \times 10^{-25} (=\hbar^6/2m^3e^6)$.

Solutions were made with both third-order and sixth-order wave functions for He and H^-.[3] The following polarizabilities and constants found for the perturbed wave functions are given in Table I.

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[3] The constants for the sixth-order wave function of H^- were kindly supplied by Mr. Ralph E. Williamson in advance of publication.