

Notice from Eq. (7) that when the deBroglie wavelength of the $A-B^-$ system becomes very small, the associative-detachment cross section can become very large. Since the relative kinetic energy of the ions produced in CO at 9.7 eV and H₂ at 3.7 eV is approximately zero, large associative-detachment cross sections are to be expected for these molecules.

Equation (7) may be employed to place lower limits on many associative-detachment cross sections of interest in astrophysics. For example, the electron attachment data of Schulz³⁵ and Rapp *et al.*²⁹ predict a lower limit of $\sim 10^{-23}$ cm² for the reaction $H^- + H \rightleftharpoons H_2^-(^2\Pi_u) \rightleftharpoons H_2 + e$ for an H⁻ energy of ~ 7 eV.

³⁵ G. J. Schulz, *Phys. Rev.* **113**, 816 (1959).

Similarly, the reaction $H^- + H \rightleftharpoons H_2^-(^2\Pi_g) \rightleftharpoons H_2 + e$ could be quite large. Such a process has been suggested³⁶ as an important intermediate reaction in the formation of stars.

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³⁶ M. R. C. McDowell, *Observatory* **81**, 240 (1961).

Angular Correlation in the Helium Atom

RONALD J. WHITE*

Theoretical Chemistry Institute, University of Wisconsin, Madison, Wisconsin

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Schwartz has shown that if the wave function for the ground state of He is developed as a perturbation series in powers of $1/Z$ and if the first-order wave function is expanded in a series of Legendre polynomials in the angle θ between the position vectors of the electrons, the contribution of the P_l component to the second-order energy behaves as l^{-4} for large l . This same behavior is noted for a model atomic system.

THE relative importance of the various angular contributions to the second-order energy for the ground state of the helium atom where $1/Z$ provides a natural perturbation parameter has been discussed by Schwartz.^{1,2} He has reported that if the first-order wave function is expanded in a series of Legendre polynomials in the angle θ between the position vectors of the electrons; the contribution of the P_l component to the second-order energy behaves as l^{-4} for large l . Lakin³ has extended the result to the total energy. This same behavior is obtained for a model atomic system.

The model atomic system will be called the Hooke's law atom. It has been studied previously by Kestner and Sinanoglu⁴ and, using perturbation theory, by White and Byers Brown.⁵ In this model the electron-nucleus interaction is assumed to be harmonic while the electron-electron interaction remains Coulombic.

For both the actual helium atom and the Hooke's law model, the equation to be solved is

$$(H_0 - E_0)\psi_1 = -(V - E_1)\psi_0, \quad (1)$$

where $V = 1/r_{12}$. Writing

$$\psi_1 = F\psi_0 \quad (2)$$

in both cases and expanding F in a Legendre series in the angle θ between the two electrons

$$F = \sum_{l=0}^{\infty} f_l(r_1, r_2) P_l(\cos\theta) \quad (3)$$

reduces the problem to an infinite set of two-dimensional equations. In both cases the equation which determines f_l is

$$\left[\nabla_1^2 + \nabla_2^2 + \frac{\partial \ln \psi_0^2}{\partial r_1} \frac{\partial}{\partial r_1} + \frac{\partial \ln \psi_0^2}{\partial r_2} \frac{\partial}{\partial r_2} \right] f_l = 2 \left[\frac{r^{< l}}{r^{> l+1}} - E_1 \delta_{l0} \right], \quad (4)$$

$$\nabla^2 \rightarrow \frac{1}{r} \frac{\partial^2 r}{\partial r^2} - \frac{l(l+1)}{r^2}.$$

* National Aeronautics and Space Administration Trainee 1965-66.

¹ C. Schwartz, *Phys. Rev.* **126**, 1015 (1962).

² C. Schwartz, in *Methods in Computational Physics*, edited by B. Alder, S. Feinbach, and M. Rotenberg (Academic Press Inc., New York, 1963), Vol. 2, p. 262.

³ W. Lakin, *J. Chem. Phys.* **43**, 2954 (1965).

⁴ N. Kestner and O. Sinanoglu, *Phys. Rev.* **128**, 2687 (1962).

⁵ R. White and W. Byers Brown, University of Wisconsin Theoretical Chemistry Institute Report No. WIS-TCI-116, 1965 (unpublished).

For the helium atom

$$\begin{aligned}\psi_0 &= \pi^{-1} \exp[-(r_1+r_2)], \\ E_1 &= 5/8;\end{aligned}\quad (5)$$

for the Hooke's law atom

$$\begin{aligned}\psi_0 &= \pi^{-3/2} \exp[-\frac{1}{2}(r_1^2+r_2^2)], \\ E_1 &= (2/\pi)^{1/2}.\end{aligned}\quad (6)$$

Now E_2 can be expanded as

$$E_2 = \sum_{l=0}^{\infty} E_2(l), \quad (7)$$

where

$$E_2(l) = \int \psi_0^2 \frac{r_1^l}{r_2^{l+1}} f_l \frac{dv_1 dv_2}{(2l+1)}, \quad l > 0. \quad (8)$$

By changing to the variables

$$\begin{aligned}s &= r_1 + r_2, \\ y &= \frac{|r_2 - r_1|}{r_1 + r_2} \lambda^{1/2}, \\ \lambda &= (l + \frac{1}{2})^2,\end{aligned}\quad (9)$$

one obtains the equation for f_l :

$$\begin{aligned}\left[s^2 \frac{\partial^2}{\partial s^2} - 2sy \frac{\partial^2}{\partial s \partial y} + y^2 \frac{\partial^2}{\partial y^2} + 2y \frac{\partial}{\partial y} - \alpha s^2 \frac{\partial}{\partial s} + \beta sy \frac{\partial}{\partial y} + \lambda \frac{\partial^2}{\partial y^2} \right. \\ \left. - \frac{4}{(1-y^2/\lambda)} \left(2y \frac{\partial}{\partial y} - s \frac{\partial}{\partial s} \right) - \frac{4(\lambda - \frac{1}{4})(1+y^2/\lambda)}{(1-y^2/\lambda)^2} \right] f_l \\ = \frac{2s e^{-2y} \exp[-(2y^3/3\lambda) - (2y^5/5\lambda^2) - \dots]}{(1-y^2/\lambda)^{1/2}},\end{aligned}\quad (10)$$

where

$$\begin{aligned}\alpha &= 2, & \text{He} \\ &= s, & \text{Hooke atom}, \\ \beta &= 2, & \text{He} \\ &= 0, & \text{Hooke atom}\end{aligned}\quad (11)$$

and where the boundary condition

$$\left. \frac{\partial f_l}{\partial y} \right|_{y=0} = 0 \quad (12)$$

must be applied to f_l since it is a symmetric function of r_1, r_2 . If f_l is expanded in inverse powers of λ

$$f_l = \lambda^{-1} f^{(-1)} + \lambda^{-2} f^{(-2)} + \dots, \quad (13)$$

Eq. (10) can be solved to give the following results:

$$f^{(-1)} = -\frac{1}{4} s e^{-2y} (1+2y) \quad (14)$$

for both the helium atom and the Hooke's law atom and

$$f^{(-2)} = -\frac{1}{4} s e^{-2y} \left[\left(-\frac{4}{3} y^4 + \frac{1}{3} y^3 + \frac{3}{2} y^2 + 2y + 1 \right) - s \left(\frac{2}{3} y^3 + y^2 + y + \frac{1}{2} \right) \right] \quad (15)$$

for the helium atom,

$$f^{(-2)} = -\frac{1}{4} s e^{-2y} \left[\left(-\frac{4}{3} y^4 + \frac{1}{3} y^3 + \frac{3}{2} y^2 + 2y + 1 \right) - s^2 \left(\frac{1}{4} y^2 + \frac{3}{8} y + \frac{3}{16} \right) \right] \quad (16)$$

for the Hooke's law atom.

The expansion $E_2(l)$ as a power series in λ^{-1} is

$$E_2(l) = -\frac{45}{256} \frac{1}{(l+\frac{1}{2})^4} \left[1 - \frac{5/4}{(l+\frac{1}{2})^2} + O\left(\frac{1}{l^4}\right) \right] \quad (17)$$

for He and

$$E_2(l) = -\frac{3}{4\pi} \frac{1}{(l+\frac{1}{2})^4} \left[1 - \frac{5/4}{(l+\frac{1}{2})^2} + O\left(\frac{1}{l^4}\right) \right] \quad (18)$$

for the Hooke's law atom.

The results reported here differ from those of Schwartz² in Eq. (15) and the second term of Eq. (17).

The similarity between the Hooke's law atom and helium indicated by Eqs. (17) and (18), and by Eq. (14), shows that the asymptotic form of f_l is independent of the nature of the electron-nucleus interaction and depends only on the Coulombic electron-electron repulsion. In the case of the Hooke's law atom, F can be obtained analytically⁵ and is a function of r_{12} only.

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