PHYSICAL REVIEW VOLUME 88, NUMBER 3 NOVEMBER 1, 1952

Convergence of Intermolecular Force Series

GLENN M. ROE
Knolls Atomic Power Laboratory, Schenectady, New York*

(Received July 11, 1952)

The second-order perturbation energy of the hydrogen molecule ion is recalculated without resorting to the mathematical approximations used by Brooks or by Unsöld. The disagreement between the corrected perturbation calculations and the exact results of Hylleraas is presumably due to the neglect of exchange forces in the initial perturbation formula and cannot be removed by Brooks' proposed scheme of arbitrarily limiting the range of integration in the matrix elements.

IN a paper with the above title,[1] Brooks proposes to modify the dipole-dipole and dipole-quadrupole contributions to the van der Waals forces between helium atoms, as calculated by second-order perturbation methods, by arbitrarily limiting the range of integration in the matrix elements to that region of space where the spherical harmonic expansion of the perturbing potential converges. He justifies this procedure by examining the mathematically similar problem of the electronic energy of the hydrogen molecule ion, where comparison can be made with exact calculations. For H_2^+, Unsöld's[2] expression for the second-order perturbation energy is

$$\Delta E_2 = -(9/4)\{(0|V^2|0)-(0|V|0)^2\}, \qquad (1)$$

where the ground-state wave function is $e^{-r}/\sqrt{\pi}$, and

$$V=(1/R)\{1-(1+r^2/R^2-2(r/R)\cos\theta)^{-\frac{1}{2}}\}, \qquad (2)$$

R being in Bohr radii. Brooks expands (2) in powers of r, neglects the second matrix element in (1), and obtains the asymptotic series

$$\Delta E_2 \cong -9\sum_{n=1}(2n+2)!/2^{2n+3}(2n+1)R^{2n+2}. \qquad (3)$$

By using his scheme of limiting the range of integration in (1) to $r<R$, he gets a revised expression

$$\Delta E_{2,\Omega} = -9\sum_{n=1}\int_0^{2R} e^{-x}x^{2n+2}dx/2^{2n+3}(2n+1)R^{2n+2}, \qquad (4)$$

which is convergent. Brooks then finds that the first term only of (4) gives better agreement with the known values of ΔE_2 than do the first two terms of (3)!

Actually, (2) can be inserted in (1) and the integrations carried out without resort to expansion in spherical harmonics. The exact result can be written in terms of the exponential-integral functions

$$\begin{aligned}\Delta E_2 = &-(9/8R)\{(2R+1)e^{-2R}\,\overline{\mathrm{Ei}}(2R)\\ &+(2R-1)e^{2R}\,\mathrm{Ei}(-2R)-2/R\}\\ &-(9/2R)(1+1/R)e^{-2R}+(9/4)(1+1/R)^2e^{-4R}. \qquad (5)\end{aligned}$$

The sum of the series (4) may be written

$$\begin{aligned}\Delta E_{2,\Omega} = \Delta E_2 &-(9/4)(1+1/R)^2e^{-4R}\\ &-(9/8R)\{(4R-2/R)e^{-2R}+(1-2R)e^{2R}\,\mathrm{Ei}(-4R)\\ &-(2R+1)e^{-2R}\log 4\gamma R\}. \qquad (6)\end{aligned}$$

Numerical values for ΔE_2 and $\Delta E_{2,\Omega}$, based on (5) and (6) rather than on an arbitrary choice of terms in (3) and (4), are given in Table I. The second column of the table gives an estimate of ΔE_2 (plus higher order perturbation energies) obtained by subtracting the first-order perturbation ΔE_1 calculated by Pauling,[3] from the exact value of the electronic energy of H_2^+ computed by Hylleraas.[4] The last column gives the values of $(\Delta E_2)_U$ computed by Unsöld,[2] who included only the first two spherical harmonics in the expansion of (2). While $\Delta E_{2,\Omega}$ appears to be a somewhat better approximation than ΔE_2, the agreement with column 2 is still very poor.

TABLE I. Various estimates of the second-order perturbation energy of H_2^+.

R	$H_2^+-\Delta E_1$	ΔE_2	$\Delta E_{2,\Omega}$	$(\Delta E_2)_U$
0.5	−0.314	−1.330	−0.312	−0.925
1.0	−0.164	−0.660	−0.263	−0.371
1.5	−0.087	−0.324	−0.171	−0.164
2.0	−0.049	−0.161	−0.101	−0.080
2.5	−0.029	−0.081	−0.058	−0.042
3.0	−0.018	−0.042	−0.033	−0.023

As pointed out by Pauling,[3] the failure of these second-order perturbation calculations to give agreement with the exact curves of Hylleraas is presumably due to the fact that Unsöld's original expression (1) is based on a hydrogen-like ground-state wave function and therefore neglects the possible effect of exchange forces. It is difficult to see how the artificial limitation of the range of integration, as proposed by Brooks, can correct for the fundamental inadequacy of (1). Thus, the improved agreement with Hylleraas which Brooks gets by his recipe appears to be a coincidence and cannot be used to justify the use of the same procedure for helium.

---

* Operated by the General Electric Company for the AEC.

[1] F. C. Brooks, Phys. Rev. **86**, 92 (1952).

[2] A. Unsöld, Z. Physik **43**, 563 (1927).

[3] L. Pauling, Chem. Revs. **5**, 173 (1928).

[4] E. A. Hylleraas, Z. Physik **71**, 739 (1931).