

201. The Dipole Moment of the Helium Hydride Molecule-ion, HeH^{2+}

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The dipole moment of the ground-state of the HeH^{2+} molecule-ion has been calculated for internuclear separations up to $5a_0$ (atomic units) from the known exact wave functions for the system.

It has not previously been possible to calculate exactly the dipole moment of any heteronuclear molecular system, but Bates and Carson¹ have recently published the exact wave functions for a number of states of the HeH^{2+} ion. Of the wave functions given, only that for the ground-state ($1s\sigma$) resembles what one generally envisages a normal bonding molecular orbital to look like, and since this system bears the same relation to heteronuclear diatomic molecules as does H_2^+ to homonuclear systems, a knowledge of the variation of dipole moment with distance is of particular interest.

The wave function is written in the form

$$\Psi(\phi, \lambda, \mu) = \Phi(\phi) \Lambda(\lambda) M(\mu)$$

where ϕ , λ , and μ are the usual confocal elliptical co-ordinates. The separate parts of the wave function are

$$\Phi(\phi) = \cos m\phi$$

$$\Lambda(\lambda) = (\lambda^2 - 1)^{\frac{1}{2}m} (\lambda + 1)^\sigma e^{-p\lambda} \sum_{s=0}^{\infty} g_s \left(\frac{\lambda - 1}{\lambda + 1} \right)^s$$

and

$$M(\mu) = e^{-p\mu} \sum_{t=m}^{\infty} f_t P_t^m(\mu)$$

where m is the orbital angular momentum quantum number and $P_t^m(\mu)$ is the associated Legendre polynomial. Bates and Carson give values of the parameters σ , p , g_s , and f_t' (not normalised) for a series of thirteen internuclear separations R in the range $0 \leq R \leq 5a_0$. The normalising constant N may be determined from the expression

$$\int \Psi^2 d\tau = N^2 \frac{R^3}{8} \int_0^{2\pi} \int_{-1}^{\infty} \int_{-1}^{+1} \Psi^2 \Lambda^2 M^2 (\lambda^2 - \mu^2) d\mu d\lambda d\phi = 1$$

and the average distance of the electron from the He^{2+} nucleus (taken as the origin of x) is

$$\int \Psi x \Psi d\tau = N^2 \frac{R^4}{16} \int_0^{2\pi} \int_{-1}^{\infty} \int_{-1}^{+1} \Phi^2 \Lambda^2 M^2 (\lambda^3 \mu + \lambda^2 - \lambda \mu^3 - \mu^2) d\mu d\lambda d\phi$$

Integration over the angle ϕ leads simply to a multiplying factor of 2π , and there remain the integrals of Λ^2 , $\lambda\Lambda^2$, $\lambda^2\Lambda^2$, $\lambda^3\Lambda^2$ over the range $1 \leq \lambda \leq \infty$ and of M^2 , μM^2 , $\mu^2 M^2$, $\mu^3 M^2$ over the range $-1 \leq \mu \leq 1$, which were evaluated numerically by using the Manchester University

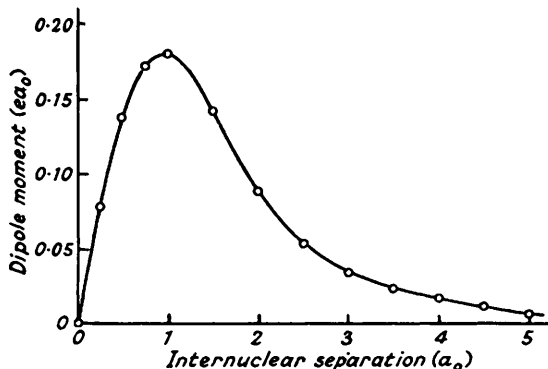
¹ Bates and Carson, *Proc. Roy. Soc.*, 1956, A, 234, 207.

Computer. The M integrals were readily obtained by using a 16-point Gaussian quadrature. The Λ integrals were transformed into the form

$$\int_0^{\infty} e^{-t} f(t) dt$$

and were then evaluated by using a modified Lagrangian quadrature³ to a high degree of precision (for the distance $R = 1$, the 7-point and 10-point calculations gave answers differing by 3 or less in the eighth decimal place, and so the 10-point quadrature was used throughout).

The results are given in the Table in the form of the directly calculated function $2\pi R^3 N^2/8$ (from which N can be found) and the derived value of the dipole moment of the system. Care has to be taken in defining the dipole moment in a charged system (*e.g.* the separation of the



positive and negative electrical centres tends to ∞ as $R \rightarrow \infty$) but where the number of electrons is equal to the difference in charge between the two nuclei, the dipole moment is given simply by $\int \Psi_x \Psi d\tau$. This is obtained by reducing each positive charge by one unit (*i.e.* in the general case by subtracting non-polar charge distributions until an equal number of positive and negative charges are left) thereby leaving a neutral system consisting of a single positive charge at the origin with an electron at an average distance $\int \Psi_x \Psi d\tau$ away from it.

$R (a_0)$	$2\pi R^3 N^2/8$	$\int \Psi_x \Psi d\tau$ (ea_0)	$R (a_0)$	$2\pi R^3 N^2/8$	$\int \Psi_x \Psi d\tau$ (ea_0)	$R (a_0)$	$2\pi R^3 N^2/8$	$\int \Psi_x \Psi d\tau$ (ea_0)
0	—	0	1.5	17.198	0.1419	3.5	206.2	0.0246
0.25	0.088306	0.0783	2.0	41.01	0.0885	4.0	302.1	0.0182
0.50	0.62969	0.1373	2.5	78.65	0.0535	4.5	423.5	0.0142
0.75	2.0564	0.1713	3.0	132.7	0.0347	5.0	573.4	0.0114
1.0	4.9123	0.1797						

The variation of dipole moment with distance takes almost the expected form³ and is shown in the Figure. It is unfortunate that the HeH²⁺ molecule is not a stable system and there may be a case from a spectroscopic point of view for repeating the whole calculation for a hypothetical molecule consisting of an electron in the field of two centres of charges $+\frac{1}{2}$ and $+1$, to see where the maximum in the dipole moment lies in relation to the minimum in the potential energy.

There is, however, an unexpectedly large disparity between the dipole moment calculated here and the value given by the L.C.A.O. approximation. At $R = 1.5a_0$ a simple linear combination of H(1s) and He(1s) functions (with variation of Z) gives an energy which is only about $\frac{1}{2}\%$ in error (*cf.* Coulson and Duncanson⁴ and Bates and Carson¹), but the corresponding dipole moment is only about $0.019ea_0$ as opposed to about $0.14ea_0$ given by the exact calculation.

³ Salzer and Zucker, *Bull. Amer. Math. Soc.*, 1949, **55**, 1004.

⁴ Herzberg, "Spectra of Diatomic Molecules," D. Van Nostrand, New York, 1950, p. 97.

⁴ Duncanson and Coulson, *Proc. Roy. Soc., A*, **165**, 90.

Note.—Since this paper was written, Moiseiwitsch and Stewart ⁵ have given exact dipole moments for six of the internuclear distances; their values agree exactly with ours. They also compare the exact values with some obtained from orbital approximations; it is clear from both sets of calculations that quite an accurate representation of the energy gives no guarantee that the wave function will lead to a dipole moment which is even of the correct order of magnitude.

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⁵ Moiseiwitsch and Stewart, *Proc. Phys. Soc.*, 1956, *A*, **69**, 480.
