A NOTE ON MOLECULAR ORBITALS

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[*Received* 17 February, *read* 8 March 1937]

One of the two principal methods of obtaining a solution of the wave equation for a molecule is that of molecular orbitals in which, as the zero-order approximation, the wave equation is taken to be separable, each electron being supposed to move in the field of the nuclei and the averaged field of the remaining electrons. This involves the solution of a Schrödinger equation for a particle moving in a potential field which is not spherically symmetrical. In general it is possible to obtain only an approximate solution of such an equation, and the purpose of this paper is to suggest an improved method of obtaining such solutions.

The equation which we have to solve is

$$\left\{\frac{\hbar^2}{2m}\nabla^2 + E - V(r,\theta,\phi)\right\}\psi = 0, \tag{1}$$

where $V(r,\theta,\phi)$ is a function which has, either accurately or approximately, the symmetry of the molecule. Now V can always be expanded in a series of surface harmonics, the coefficients being functions of r. If the functions of r are linearly independent (they can always be made so if necessary by taking one or more terms of the series together), then each is multiplied into a surface harmonic which must have the same symmetry as V. This condition may greatly reduce the number of terms in the expansion of V. For instance, it can be shown that if V has octahedral symmetry there is no harmonic of degree lower than four (except the zero-order one) which has the same symmetry. The types of harmonic that can occur in the expansion for molecules having various kinds of symmetry have been given by Bethe*. We shall approximate to V by taking only the first two terms in the expansion, that is we assume that

$$V(r,\theta,\phi) = V_0(r) + V_1(r)\,P(\theta,\phi), \tag{2}$$

where $P(\theta,\phi)$ is the surface harmonic of lowest order having the same symmetry as V. Equation (1) then becomes

$$\left[\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + E - V_0(r) + \frac{\hbar^2}{2m}\frac{1}{r^2}\left\{\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right\} - V_1(r)P(\theta,\phi)\right]\psi = 0. \tag{3}$$

* *Ann. Physik*, 3 (1929), 133.

https://doi.org/10.1017/S0305004100019599 Published online by Cambridge University Press

The usual way of solving an equation of this type is to treat $V_1(r)\,P(\theta,\phi)$ as a perturbation, but a more accurate solution can be obtained by a variation method provided we know the solution of the equation

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}+W+kP(\theta,\phi)\right]g=0, \tag{4}$$

for a suitable range of values of the parameter k. Solutions of equations of the type (4) have, in fact, been given for the case when $P(\theta,\phi)$ is a function of θ only* (as in a linear molecule) and also when $P(\theta,\phi)$ has tetrahedral†, or octahedral‡ symmetry.

We assume that $$\psi=f(k,r)\,g(k,\theta,\phi), \tag{5}$$

where k is a parameter which we shall choose so that the energy is a minimum, and $g(k,\theta,\phi)$ satisfies equation (4). If we substitute this value for ψ in equation (3) and use equation (4), we have

$$\left[\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+E-V_0(r)-\frac{\hbar^2}{2m}\frac{W}{r^2}-\left(V_1(r)+\frac{\hbar^2}{2m}\frac{k}{r^2}\right)P(\theta,\phi)\right]f(k,r)\,g(k,\theta,\phi)=0, \tag{6}$$

and hence, multiplying by $g(k,\theta,\phi)$ and integrating over the surface of a sphere, we deduce that

$$\left[\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+E-V_0(r)-\frac{\hbar^2}{2m}\frac{1}{r^2}(W+k\bar{P})-\bar{P}V_1(r)\right]f(k,r)=0, \tag{7}$$

where $$\bar{P}=\int_0^{\pi}\int_0^{2\pi}|\,g(k,\theta,\phi)\,|^2\,P(\theta,\phi)\sin\theta\,d\theta\,d\phi,$$

$g(k,\theta,\phi)$ being normalized in such a way that

$$\int_0^{\pi}\int_0^{2\pi}|\,g(k,\theta,\phi)\,|^2\sin\theta\,d\theta\,d\phi=1.$$

Now§ if we consider the equation

$$\left[\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\left(\frac{1}{\sin\theta}\right)^2\frac{\partial^2}{\partial\phi^2}+W+(k+\delta k)\,P(\theta,\phi)\right]g=0,$$

and treat the term in δk as a perturbation, we find that

$$W(k+\delta k)=W(k)-\bar{P}\,\delta k+O\{(\delta k)^2\},$$

and hence $$\bar{P}=-\frac{dW}{dk}.$$

* Stern, *Proc. Roy. Soc.* 130 (1930), 551.
† Cundy, not yet published.
‡ Devonshire, *Proc. Roy. Soc.* 153 (1936), 676.
§ Cf. Lennard-Jones and Pike, *Trans. Faraday Soc.* 30 (1934), 837, eq. (18).

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Equation (7) therefore becomes

$$\left[\frac{\hbar^2}{2m}\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+E-V_0(r)+V_1(r)\frac{dW}{dk}-\frac{\hbar^2}{2m}\frac{1}{r^2}\left(W-k\frac{dW}{dk}\right)\right]f(k,r)=0, \qquad (8)$$

which contains only known functions of k. Since it is an equation in a single variable it can always be solved, by mechanical means if necessary, for any value of k, and we can then choose k so that the energy is a minimum.

If we denote by $V(k,r)$ the potential

$$V_0(r)-V_1(r)\frac{dW}{dk}+\frac{\hbar^2}{2m}\frac{1}{r^2}\left(W-k\frac{dW}{dk}\right),$$

then by applying the perturbation theory we infer that

$$\begin{aligned}\frac{dE}{dk} &= \int_0^\infty f^*(k,r)\{\partial V(k,r)/\partial k\}f(k,r)\,r^2\,dr \\ &= -\frac{d^2W}{dk^2}\int_0^\infty f^*(k,r)\left\{V_1(r)+\frac{\hbar^2}{2m}\frac{k}{r^2}\right\}f(k,r)\,r^2\,dr, \qquad (9)\end{aligned}$$

where $f(k,r)$ is normalized in such a way that

$$\int_0^\infty f^*(k,r)f(k,r)\,r^2\,dr=1.$$

Hence the required value of k is given by the equation

$$\frac{\hbar^2}{2m}k\int_0^\infty f^*(k,r)\frac{1}{r^2}f(k,r)\,r^2\,dr=-\int_0^\infty f^*(k,r)\,V_1(r)f(k,r)\,r^2\,dr. \qquad (10)$$

We note that it is sufficient to know the eigenvalues, and not the wave functions also, of equation (4) in order to obtain the eigenvalues of equation (3). If, however, we do know the eigenfunctions of equation (3), then the value of ψ given by equation (5) should be a reasonable approximation to the eigenfunction of the complete equation.

SUMMARY

A method of obtaining an approximate solution of Schrödinger's equation with a non-central field of force is given for the case when a solution of a similar equation involving the angular coordinates only is known.

In conclusion I should like to thank Prof. J. E. Lennard-Jones, F.R.S., for suggesting the problem and for his continued interest in it, and also the Department of Scientific and Industrial Research for a grant.

https://doi.org/10.1017/S0305004100019599 Published online by Cambridge University Press