I INTRODUCTION

A very important function of quantum mechanical calculations is to obtain the energies of chemical systems. At best, due to mathematical complexities, this can be done only approximately (except for very simple systems). For an exact solution, it is necessary to find the eigenfunctions, (Ψ_i), of the Schroedinger wave equation:

$$H\Psi = E\Psi$$

or,

$$E = \frac{\int \Psi^* H \Psi \, d\tau}{\int \Psi^* \Psi \, d\tau}$$

where the integration is carried out over all space, E stands for the energy, and H for the Hamiltonian operator.

$$H = - \sum_{\text{electrons}} (1/2)\nabla^2 + V_{nn} + V + M^{(1)} \qquad \text{(I-1)}$$

where the kinetic energy of the nuclei has been omitted (as the nuclei will be assumed fixed), the first term represents the kinetic energy of the electrons, and V_{nn}, V, and M are the contributions to the potential energy arising from nuclear, nuclear-electronic, and electronic interactions, respectively.

The Hamiltonian has been given in atomic units. These units will be used throughout:

$E_\circ$ = 27.2 electron volts

$a_\circ$ = 0.5292 Å

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(1) See, for example, H. Eyring, J. Walter, and G.E. Kimball, Quantum Chemistry, Wiley, New York, 1944, p. 190

~~Substituting, and, for~~ convenience, using K for $-1/2\nabla^2$, the energy integral is of the form:

$$(\Psi|H|\Psi) = \sum_{\substack{\text{single}\\ \text{electrons}}} (\Psi|K|\Psi) + \sum_{\substack{\text{single}\\ \text{electrons}}} (\Psi|V|\Psi) + \sum_{\substack{\text{electron}\\ \text{pairs}}} (\Psi|M|\Psi) + V_{nn} \qquad (I\text{-}2)$$

where V is summed over all nuclei. In the above, Dirac notation has been used:

$$(\Psi|X|\Psi) = \int_{\substack{\text{all}\\ \text{space}}} \Psi^* X \Psi \, d\tau$$

X being any operator. (Frequently, for simplicity, X will be used to represent the energy integral; in those cases, it will not be in combination with Ψ).

For obtaining approximate solutions, the standard procedure is the variation method. It can be shown that, for any function Ψ,

$$\frac{(\Psi|H|\Psi)}{(\Psi|\Psi)} \geq E^{(1)} \qquad (I\text{-}3)$$

Therefore, as $\Psi(p_1, p_2, \ldots)$ is minimized by a variation of parameters $(p_1, p_2, \ldots)$, the above integrals will approach the energy.

An attempt to find a set of functions necessitating only relatively simple calculations, while at the same time retaining reasonable accuracy, will be dicussed here. The molecular orbital method will be used.

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(1) See, for example, Eyring, Walter, and Kimball, <u>Quantum Chemistry</u>, New York, 1944, p.99 ff.

Provisionally neglecting exchange effects, the molecular orbital method attempts to find the best product wave function,

$$\Psi = \phi_a(1)\phi_b(2)\cdots \qquad (I-4)$$

where, as usual, $\phi_a, \phi_b, \ldots$ stand for one-electron functions, and (1),(2),... for the various electrons.

In choosing these wave functions, the parameters can be divided into two sets:

a) The coordinates of the center of ϕ

b) Shape parameters

Essentially, however, a knowledge of the wave functions is of secondary importance. For obtaining the energy, it is the integrals K, V, and M which are needed. These depend on the same parameters as the wave functions, as the parameters are not affected by integration. Thus, in practice, the minimization process can be carried out in two steps, corresponding to the two sets of parameters:

a) For a fixed shape, variation of the center positions

b) Variation of the shape

The first step is simply the solution of a problem in electrostatics, namely the determination of the equilibrium position of a set of clouds (of charge density $\phi^*\phi$) and point charges. The kinetic energy is not affected by a change in the position of ϕ: as the integration is over all space, $\int \Psi^* \nabla^2 \Psi \, d\tau$ is invariant to a translation.

The next step is the variation of the shape.

As far as the potential energy is concerned, at large distances, it does not depend on the shape: all ϕ give the simple $1/r$ Coulomb law, where r is the separation between the particles. However, at small separations, there is a shape dependence. In order to obtain a simple set of parameters, the following assumption has been made: the shape dependence is mainly a function of how diffuse the cloud is, ie. what its size is. It is then sufficient to use only spherically symmetric clouds. This still leaves the possibility of different charge densities. Both this and the size assumption will be discussed again later, and the latter partly justified by example.

Spherically symmetric clouds appear satisfactory also for the kinetic energy. For minimum total energy, it is desireable that, for a given potential energy, the kinetic energy be as low as possible. It will be shown, by the Uncertainty Principle, that this is the case for spherical symmetry.

For an ellipsoid:

$$\overline{x^2} : \overline{y^2} : \overline{z^2} = a^2 : b^2 : c^2$$

let $\bar{R}$ = root mean square radius

$$\overline{R^2} = \overline{x^2} + \overline{y^2} + \overline{z^2}$$

$$\overline{x^2} = \frac{a^2\overline{R^2}}{a^2 + b^2 + c^2}$$

, with similar expressions for

the other average values ($\overline{y^2}$ and $\overline{z^2}$).

Let Δx and Δp be the respective root mean squares of the deviations of x and p from their mean values, where p is the momentum. Then, by the Heisenberg Uncertainty Principle, [2]

$$\Delta x \, \Delta p_x \geq h/4\pi$$

or, for $\bar{x} = \overline{p_x} = 0$

$$\overline{x^2} \; \overline{p_x{}^2} \geq h^2/16\pi^2$$

thus,

$$\overline{p_x{}^2} \geq \frac{h^2}{16\pi^2 R^2} \, \frac{a^2 + b^2 + c^2}{a^2}$$

with similar expressions for $\overline{p_y{}^2}$ and $\overline{p_z^2}$.

$$K = (1/2m)\overline{p^2}$$

$$\geq \frac{h^2}{32\pi^2 mR^2} (a^2 + b^2 + c^2)(1/a^2 + 1/b^2 + 1/c^2)$$

For minimum kinetic energy, $\frac{\partial K}{\partial a} = \frac{\partial K}{\partial b} = \frac{\partial K}{\partial c} = 0$

Thus, $2a(1/a^2 + 1/b^2 + 1/c^2) - (2/a^3)(a^2 + b^2 + c^2) = 0$

or, $a^4(1/a^2 + 1/b^2 + 1/c^2) = a^2 + b^2 + c^2$

Similarly, $b^4(1/a^2 + 1/b^2 + 1/c^2) = a^2 + b^2 + c^2$

$c^4(1/a^2 + 1/b^2 + 1/c^2) = a^2 + b^2 + c^2$

Dividing these equations by pairs,

$$a^4 = b^4 = c^4$$

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(2) E. Kemble, Fundamental Priciples of Quantum Mechanics McGraw-Hill, New York, 1937

or, for real roots,

$$a = b = c$$

Thus, for minimum energy, the charge distribution should be spherically symmetric.

Since the kinetic energy could approach infinity (for example for $a=0$, b or $c \neq 0$), whereas the energy for $a=b=c$ remains finite, the above expression actually gives a minimum.

For spherical symmetry,

$$K \geq \frac{9h^2}{32\pi^2 m\overline{R^2}}$$

or, in atomic units $(a_o = h^2/4\pi^2 me^2\ ,\ \ E_o = e^2/a_o)$

$$K \geq (9/8\overline{R^2}) \qquad (I\text{-}5)$$

The kinetic energy as calculated by integration might come out somewhat larger than this; however, for minimum energy, it is desireable that it be as low as is consistent with this Principle.