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Application of the Virial Theorem to Approximate Molecular and Metallic Eigenfunctions

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Fock showed that the virial theorem is automatically satisfied for any quantum-mechanical system whose potential is a homogenous function of the coordinates if a scale factor is introduced into the approximate charge distribution and varied so as to give the lowest energy. In this paper, we extend Fock's treatment to problems involving molecules or metals where it is customary to treat the internuclear separations as parameters. The introduction and variation of the scale factor requires very little additional work and results in considerable improvement in the physical properties. The Heitler-London-Sugiura charge distribution for molecular hydrogen has a mean potential energy, $V=-52.98$ ev; a mean kinetic energy, $T=22.79$ ev; and a total energy, $E=V+T=-30.20$ ev. When the scale factor is inserted into the eigenfunction and varied to form the Wang function: $E=-T=\frac{1}{2}V=-30.83$ ev and the virial theorem is satisfied. The total energy is improved by only 0.63 ev but the potential energy is improved by 8.67 ev and the kinetic energy by 8.04 ev. The eigenfunction for the diatomic hydrogen ion, $\Psi=N[\exp(-r_a)+\exp(-r_b)]$ where N is the normalization factor and r_a and r_b are the distances of the electrons to nuclei a and b, respectively, is another example where the scale factor results in striking improvement in the mean potential and kinetic energies. The James and Coolidge function for molecular hydrogen almost satisfies the virial theorem since $\frac{1}{2}V=-31.680$ ev and $-T=-31.588$ ev. When the scale factor, $s=1.0029$, is introduced, we obtain $E=\frac{1}{2}V=-T=-31.772$ ev. If the mean potential and kinetic energies, V_1 and T_1 respectively, are known for one nuclear separation, R_0, then on the introduction and variation of the scale factor, a lower energy is obtained for the internuclear separation, $R=-2R_0T_1/V_1$, for which $E=-T=\frac{1}{2}V=-\frac{1}{4}V_1^2/T_1$.

A FEW years ago, Professor Slater[1] pointed out that the virial theorem applies to molecular systems and that it offers a new principle to use in obtaining satisfactory charge distributions. In this paper, we develop a simple method for modifying the approximate charge distributions to satisfy the virial theorem and we find that considerable improvement in the molecular properties results. Fock[2] showed that the virial theorem is automatically satisfied for any quantum mechanical system whose potential is a homogenous function of the coordinates if a scale factor is introduced into the approximate charge distribution and varied so as to give the lowest energy. The form which Fock developed is useful for atomic problems, but his theorem requires extension for problems involving molecules or metals where it is customary to treat the internuclear separations as parameters.

In this paper, we consider only those approximate molecular or metallic eigenfunctions for the ground state which do not involve the internuclear distances explicitly but only implicitly through the electronic coordinates. These eigenfunctions are functions only of the separations of the electrons from the nuclei and from each other. There is no serious loss in generality as a result of this condition since any approximate eigenfunction can be put into this form by replacing the internuclear distances, R, in the eigenfunction by R_0, the values of the internuclear separations for a particular configuration. Let $\Psi_1(r, R)$ be an approximate eigenfunction satisfying this condition where r is symbolic for the electronic coordinates. The scale factor, s, is introduced into the charge distribution in such a way that each electronic distance is multiplied by s whilst the internuclear separations remain unchanged. Thus:

$$\Psi_s(r, R)=s^{\frac{1}{2}3n}\Psi_1(sr, R). \tag{1}$$

Here n is the number of electrons in the system. The subscripts s and 1 indicate that the eigenfunctions are for the scale factors s and 1, respectively. The effect of s is to shrink the electronic charge distribution closer to the nuclei just as though these nuclei increased their effective charge by this factor. The approximate eigenfunctions with the scale factors are related to the approximate eigenfunctions without the scale factors but for which the internuclear separations are expanded by s. For each elec-

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[1] J. C. Slater, J. Chem. Phys. **1**, 687 (1933).

[2] V. Fock, Zeits. f. Physik **63**, 855 (1930).

tronic configuration, r, with the internuclear separations, R, there is a corresponding geometrically similar configuration for the nuclear separations, sR, such that the electronic separations are $r'=sr$. Because of the assumption which we have made as to the functional form of Ψ:

$$\Psi_s(r, R)=s^{\frac{1}{2}3n}\Psi_1(r', sR). \qquad (2)$$

The mean value of the (electronic) kinetic energy, $T_s(R)$, is given by the relation:

$$T_s(R)=-\frac{h^2}{8\pi^2 m}\int\bar{\Psi}_s(r, R)\sum_{\text{electrons}}\Delta_i\Psi_s(r, R)d\tau. \qquad (3)$$

Now using (2) and making the substitution of variables $r'=sr$, it follows that:

$$T_s(R)=s^2T_1(sR). \qquad (4)$$

The mean potential energy of the system, $V_s(R)$, is given by the relation:

$$V_s(R)=\int\bar{\Psi}_s(r, R)[U_{ee}+U_{en}+U_{nn}]\Psi_s(r, R)d\tau, \qquad (5)$$

where

$$U_{ee}=\sum_{\substack{\text{electron}\\ \text{pairs}}} e^2/r_{ij},\quad U_{en}=-\sum_{\substack{\text{electrons, }i,\\ \text{and nuclei, }\alpha}} e^2/r_{i\alpha},$$

$$U_{nn}=\sum_{\substack{\text{nuclear}\\ \text{pairs}}} e^2/r_{\alpha\beta}.$$

Again using (2) and making the substitution $r'=sr$, it follows that:

$$V_s(R)=sV_1(sR). \qquad (6)$$

The total energy of the molecule, $E_s(R)$, is of course the sum of the mean potential and kinetic energies:

$$E_s(R)=T_s(R)+V_s(R)=s^2T_1(sR)+sV_1(sR). \qquad (7)$$

Usually there will be values of s different from unity for which the energy of the system is improved. The best value of s for a particular nuclear configuration can be found from the condition that the energy is stationary for this value of the scale factor:

$$0=\left(\frac{\partial E_s(R)}{\partial s}\right)_R=2sT_1(sR)+V_1(sR)$$
$$+R\left[s^2\frac{dT_1(sR)}{d(sR)}+s\frac{dV_1(sR)}{d(sR)}\right]. \qquad (8)$$

For the best value of R we have the additional condition that the energy be stationary with respect to variations in the internuclear separations, R:

$$0=\left(\frac{\partial E_s(R)}{dR}\right)_s=s\left[s^2\frac{dT_1(sR)}{d(sR)}+s\frac{dV_1(sR)}{d(sR)}\right]. \qquad (9)$$

Combining (8) and (9) we see that for the best value of the internuclear distances, the best value of s is

$$s=-\tfrac{1}{2}V_1(sR)/T_1(sR), \qquad (10)$$

for which the lowest value for the total energy is

$$E_s(R)=-\tfrac{1}{2}V_1(sR)^2/T_1(sR). \qquad (11)$$

The virial theorem is satisfied by this charge distribution since:

$$E_s(R)=-T_s(R)=\tfrac{1}{2}V_s(R), \qquad (12)$$

when (10) is substituted into (4) and (6). Therefore we have the general theorem: *If the approximate charge distribution is expanded or contracted, the size which corresponds to the lowest energy gives the proper ratio between potential and kinetic energy.*

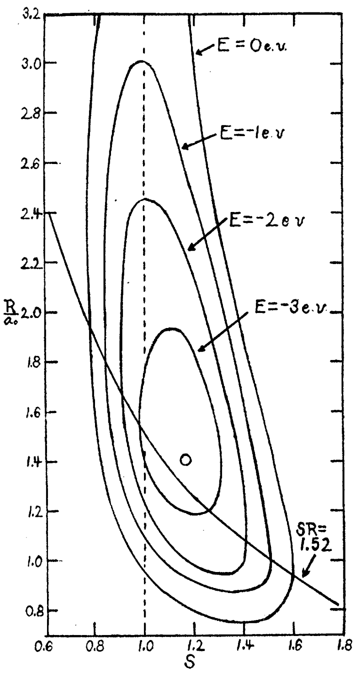

FIG. 1. The energy of H_2 as a function of R and s.

A simple example will illustrate the dependence of the molecular energy on the scale factor. Consider the Heitler-London-Sugiura[3, 4] eigenfunction for molecular hydrogen:

$$\Psi_1(r, R) = N[\exp(-r_{a1} - r_{b2}) + \exp(-r_{a2} - r_{b1})]. \quad (13)$$

Here N is the normalizing factor; r_{a1}, r_{b1}, r_{a2}, r_{b2} are the separations of electron 1 from nuclei a and b and similarly for electron 2. For the lowest energy, the hydrogen nuclei are separated a distance of $R = 1.52a_0$ where a_0 is the radius of the first Bohr orbit. Here:

$$E_1(R) = -30.20 \text{ ev},$$
$$-T_1(R) = -22.79,$$
$$\tfrac{1}{2}V_1(R) = -26.49.$$

These three quantities should be equal. Since they are not equal, the virial theorem is not satisfied in this case. This situation can be remedied by introducing the scale factor s into the eigenfunction to make this Heitler-London-Sugiura function into a Wang[5] eigenfunction.

$$\Psi_s(r, R) = N'[\exp(-sr_{a1} - sr_{b2}) + \exp(-sr_{a2} - sr_{b1})]. \quad (14)$$

Here N' is the new normalizing factor. Fig. 1 shows the energy as a function of both s and R. The lowest energy is for the point $s = 1.166$ and $R = 1.41a_0$ and this point is indicated in the figure by the small circle. For this configuration:

$$E_s(R) = -T_s(R) = \tfrac{1}{2}V_s(R) = -30.83 \text{ ev}.$$

Thus the variation of the scale factor has improved the total energy by only 0.63 ev but the mean kinetic energy is improved by 8.04 ev and the mean potential energy by 8.67 ev. This large change in potential and kinetic energies is an indication of the improvement to be expected in the other molecular properties.

The improvement in the potential and kinetic energies for the diatomic hydrogen ion, H_2^+, will show that the above is not an exceptional case. Consider as eigenfunction for H_2^+ the simple sum of atomic functions which Pauli[6] used in classical quantum mechanics:

$$\Psi_1(r, R) = N[\exp(-r_{a1}) + \exp(-r_{b1})]. \quad (15)$$

For the best internuclear separation

$$E_1(R) = -15.30 \text{ ev},$$
$$-T_1(R) = -10.37 \text{ ev},$$
$$\tfrac{1}{2}V_1(R) = -12.84 \text{ ev},$$

Now introducing the scale factor to form the Finkelstein and Horowitz[7] function:

$$E_s(R) = -T_s(R) = \tfrac{1}{2}V_s(R) = -15.90 \text{ ev}$$

where $s = 1.238.$

Here the improvement in the total energy is only 0.60 ev but there is a decrease of 6.12 ev in the potential energy and an increase of 5.53 ev in the kinetic energy.

In many molecular problems the computation of the energy is very laborious for each nuclear configuration. For these cases it would be difficult to construct the whole surface for energy as a function of s and R. However, knowing the mean potential and kinetic energy for just one nuclear configuration, R_0, we can use Eq. (7) to determine the energy along the rectangular hyperbola, $sR = R_0$, in the s, R diagram. Along this hyperbola the lowest energy is given for $s = -\tfrac{1}{2}V_1(R_0)/T_1(R_0)$ at the internuclear separation $R = R_0/s$. For this value of s the virial theorem holds and

$$E_s(R) = -T_s(R) = \tfrac{1}{2}V_s(R) = -\tfrac{1}{4}V_1(R_0)^2/T_1(R_0). \quad (16)$$

This $E_s(R)$ is always lower than $E_1(R_0)$ but it is not necessarily lower than $E_1(R)$ or $E_{s'}(R)$ where s' is some other value of the scale factor and R is the same internuclear separations. If R_0 is chosen as the best separation of the nuclei when the scale factor is unity, the point of lowest energy along the hyperbola will come close to but in general will not coincide with the configuration having both the best R and the best s. This is because the term in brackets in Eq. (8) does not vanish. Thus for the Wang eigenfunction for H_2 the best value of R is $1.52a_0$ when $s = 1.00$. Following along the hyperbola $sR = 1.52$ (see Fig. 1) we find the lowest energy

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[3] Heitler and London, Zeits. f. Physik **44**, 455 (1927).

[4] Y. Sugiura, Zeits. f. Physik **45**, 484 (1927).

[5] S. C. Wang, Phys. Rev. **31**, 579 (1928).

[6] Pauli, Ann. d. Physik **68**, 177 (1922); also the Dissertation of K. F. Niessen, Utrecht University (1922).

[7] Finkelstein and Horowitz, Zeits. f. Physik **48**, 118 (1928).

for $s=1.162$ at which $E_s(R)=-30.79$ ev and $R=1.30a_0$. This is close to the best point on the entire energy surface for which it will be remembered that $s=1.166$, $E_s(R)=-30.83$ ev, and $R=1.41a_0$.

To show how the proper ratio of the potential to the kinetic energy can be obtained easily in a complicated case, we consider the thirteen term eigenfunction of James and Coolidge[8] for H_2. Here:

$$E_1(R)=-31.772\text{ ev},$$
$$-T_1(R)=-31.588\text{ ev},$$
$$\tfrac{1}{2}V_1(R)=-31.680\text{ ev}.$$

This charge distribution is truly excellent but the physical properties of even this eigenfunction can be improved by the introduction of the scale factor, $s=1.0029$, for which

$$E_s(R)=-T_s(R)=\tfrac{1}{2}V_s(R)=-31.772\text{ ev}.$$

The improvement in the total energy is only 0.0003 ev and hence negligible, but the mean potential and the mean kinetic energies are each improved by 0.184 ev.

N. Rosen[9] has discussed the variation of the best value of the scale factor with internuclear distance. For large separations s is less than unity so that the charge distributions are expanded. This is due of course to the charges being pulled towards the nucleus of the approaching atom. For smaller separations s is greater than unity and the charges are contracted. If the nuclei coalesce s assumes a finite value larger than for the separated atoms. This variation of s with internuclear separation makes it difficult to determine the energy as a function of the internuclear separations using the best value of s for each separation. Because of this difficulty, Wang computed the fundamental vibration frequency of H_2 on the assumption that s remains equal to 1.166 over the whole range of internuclear separations. A study of Fig. 1 will show that the energy as a function of R varies much more rapidly along the line $s=1.166$ than along the curve of best values of s. Therefore a more accurate calculation of the fundamental vibration frequency would decrease Wang's value of 4900 cm^{-1} to a value more in agreement with the experimental observation of 4260 cm^{-1}.

From Eq. (2), it follows that any molecular property which is proportional to the qth power of the electronic coordinates is multiplied by s^{-q} when the scale factor is introduced. Thus we have shown that very little additional work is required to introduce a scale factor into a molecular or metallic charge distribution and the physical properties of the system are considerably improved thereby.

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[8] James and Coolidge, J. Chem. Phys. **1**, 825 (1933).

[9] N. Rosen, Phys. Rev. **38**, 2099 (1931).