FORCES AND STRESSES IN MOLECULES

by

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FORCES AND STRESSES IN MOLECULES

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GENERAL INTRODUCTION:

Many of the problems of molecular structure are concerned essentially with forces. The stiffness of valence bonds, the distortions in geometry due to the various repulsions and attractions between atoms, the strength of the tendencies of valence bonds to occur at certain definite angles with each other, are some examples of the kind of problem in which the idea of force or stress is paramount. Usually these problems have been considered through the agency of energy, and its changes on changing configurations of the molecule. The reason for this indirect attack through energy, rather than the more qualitatively illuminating one by considerations of force is perhaps twofold. First, it is probably thought that force is a quantity that is not easily described or calculated by wave mechanics, while energy is, and second, the first molecular problems to be solved have been the band spectra, strictly a problem of energy as such.

It is the purpose of this thesis to show that forces are almost as easy to calculate directly as energy is, and that the equations are quite as easy to interpret. Furthermore, there exists for quantum mechanics a stress tensor of molecular forces, analagous to the Maxwell stress tensor of electric and magnetic forces. The thesis is, thus, very naturally divisible

into two parts. The first will deal with considerations of the forces on the atoms of a molecule, and the second part with the form of the stress tensor in the space in and around a chemical molecule.

Unfortunately, time did not permit the actual computation of these forces and stresses for any real case, rather only the form of the equations for force and stress have been worked out. The following is thus to be looked upon as a description of a method of obtaining information about molecules, few actual computations having been performed.

PART I FORCES

A usual method of calculating inter-atomic forces runs somewhat as follows:

For a given fixed separation of the nuclei, the energy of the entire system (electrons and nuclei) is calculated. This is done by the variation method or other perturbation schemes. This entire process is repeated for a new nuclear position, and the new value of the energy calculated. In this way, a plot of energy vs. position of the nuclei is obtained. The force on a nucleus is, of course, the slope of this curve.

Now the following method is one to obtain the forces at a given configuration, knowing only the configuration and not requiring the calculations at neighboring configurations. That is, it permits a calcula-

tion of the slope of the energy curve as well as its value, for any particular configuration.

It is to be emphasized that this permits a considerable saving of labor of calculations. To obtain force under the old scheme the energy needed to be calculated for at least two (or three, if accuracy is to be insured) different and neighboring configurations. Each point requires calculating the wave functions for the entire system. In this new method, only one configuration, the one in question, need have the wave functions computed in detail. Thus, the labor is approximately half as great.

The method is based on the following theorem: The force on any nucleus (considered fixed) in any system of nuclei and electrons is just the classical electrostatic attraction exerted on the nucleus in question by other nuclei and by the electron charge density distribution. The electron charge distribution is of course given by $\rho(x) = \sum_i \rho_i(x)$ if $\rho_i(x)$ is the charge distribution due to one electron i, the usual expression for which is $\int \bar{i} \int \psi\psi^* d\tau d\tau$, where ψ is the wave function for all the electrons, and here, as later, $\int \bar{i} \int$ will mean integral over all coordinates of all electrons except those of electron i.

This is an interesting result in that it indicates another way of looking at wave mechanics. All forces on nuclei, etc. can be considered as purely

classical attractions involving Coulomb's law. The electron cloud distribution, however, is prevented from collapsing by obeying Schrodinger's equation. In these considerations the nuclei are considered as mass points held fixed in position.

I have applied the theorem to obtain an expression for van der Waals forces, and also to polarizability by considering the force on an atom in a non-uniform field.

Because it permits one to get an independent value of the slope of the energy curve, the theorem might increase the accuracy in the calculation of such curves, since a knowledge of both value and slope permit a more accurate curve to be drawn than just knowledge of value. Further, to obtain normal separation of atoms it is necessary to obtain a minimum for the energy curve. This usually requires accurate calculations of the energy at several points around the approximate minimum. If the slope of the energy is calculated independently, however, by means of the force theorem, it is a comparatively simple job to obtain accurately the position of zero force.

It is also quite useful for qualitative considerations of atomic forces. It becomes quite clear why the strongest and most important forces arise when there is a concentration of charge between two nuclei. The nuclei on each side of the concentrated charge are

each strongly attracted to it. Thus, they are in effect attracted toward each other. In a H_2^+ molecule, for example, the antisymmetric solution, because it must be zero exactly between the two H atoms cannot concentrate charge between them. The symmetric solution, however, can easily permit charge concentration between the nuclei, and hence it is only the solution that is symmetrical in the two electrons that leads to strong attraction, and the formation of the molecule, as is well known.

Sometimes the atomic wave function of a single atom is distributed in space in such a manner as to have large concentrations of charge situated in certain positions relative to each other. Examples are the two perpendicular concentrations arising from the p electrons in the oxygen atom, or the four tetrahedrally arranged places of higher charge density in the carbon atom. A new atom, being brought up to this, will try to overlap its charge with that of the central atom, for otherwise it would not be strongly attracted. That is, of course, the generally accepted explantion of directed valence in the atomic-orbital method of approach.* It is seen here as obvious that concentrations of charge between atoms leads to strong attractive forces, and hence, are properly called valence bonds.

*Quantum Theory of Valence, J. H. Van Vleck and A. Shorman Rev. Mod. Phys. 7, 167 (1935)

2. EQUATION FOR THE FORCES

Let λ be one of any number of parameters which specify nuclear positions. For example, λ might be the x component of the position of one of the nuclei. A force f_λ is to be associated with λ in such a way that $f_\lambda d\lambda$ measures the virtual work done in displacing the nuclei $d\lambda$. This will define the force only when the molecule is in a steady state, of energy U, for then we can say $f_\lambda = -\frac{\partial U}{\partial \lambda}$. In the non-steady state we have no sure guide to a definition of force. For example, if $\bar{U} = \int \psi^* H \psi \, d\tau$ be the average energy of the system we might define

$$f_\lambda' = -\frac{\partial(\bar{U})}{\partial \lambda} \qquad (1)$$

Or again we might take f_λ to be the average of $-\frac{\partial H}{\partial \lambda}$ or

$$f_\lambda = -\overline{\frac{\partial H}{\partial \lambda}} = -\int \psi^* \frac{\partial V}{\partial \lambda} \psi \, d\tau \qquad (2) \quad \text{since} \quad \frac{\partial H}{\partial \lambda} = \frac{\partial V}{\partial \lambda}.$$

I shall prove that in the steady state case both these definitions of force become exactly equivalent, and equal to $-\frac{\partial U}{\partial \lambda}$ the slope of the energy curve. Since (2) is far simpler than (1), we shall define force by (2) in general. In particular it gives a simple expression for the slope of the energy curve.

Thus we shall now prove, when $H\psi = U\psi$ and $\int \psi\psi \, d\tau = 1$ (where we take ψ real, an inessential simplification) that $\frac{\partial U}{\partial \lambda} = \int \psi\psi \frac{\partial V}{\partial \lambda} d\tau$.

But, $U = \int \psi H \psi \, d\tau = -\int \psi \frac{h^2}{8\pi^2 m} \nabla^2 \psi \, d\tau + \int \psi V \psi \, d\tau$

Whence, $-\frac{\partial U}{\partial \lambda} = \frac{h^2}{8\pi^2 m}\left\{\int \frac{\partial \psi}{\partial \lambda} \nabla^2 \psi + \int \psi \nabla^2 \frac{\partial \psi}{\partial \lambda}\right\} - 2\int \frac{\partial \psi}{\partial \lambda} V \psi \, d\tau - \int \psi\psi \frac{\partial V}{\partial \lambda} d\tau$

Now, Green's theorem states that $\int\{\psi\nabla^2\phi-\phi\nabla^2\psi\}d\tau=0$ so the second term on the right can be rearranged to equal the first and we arrive at the relation:

$$-\frac{\partial U}{\partial\lambda}=2\int\frac{\partial\psi}{\partial\lambda}\left\{\frac{h^2}{8\pi^2 m}\nabla^2\psi-V\psi\right\}d\tau-\int\psi\psi\frac{\partial V}{\partial\lambda}d\tau$$

$$=2\int\frac{\partial\psi}{\partial\lambda}U\psi\,d\tau-\int\psi\psi\frac{\partial V}{\partial\lambda}d\tau=U\frac{\partial}{\partial\lambda}\int\psi\psi\,d\tau-\int\psi\psi\frac{\partial V}{\partial\lambda}d\tau$$

or $f_\lambda'=-\int\psi\psi\frac{\partial V}{\partial\lambda}d\tau=f_\lambda$ (2) in the steady state case, the first term vanishing since $\frac{\partial}{\partial\lambda}\int\psi^2 d\tau=\frac{\partial}{\partial\lambda}(1)=0$ This proves that (2) is a simple expression for calculating the slope of the energy curve if the wave functions are known.

3. EFFECT OF PERTURBATIONS

Next let us consider the way the force acts under a perturbation, by the regular Schrodinger perturbation method. Let V_0 be the unperturbed potential, P the perturbation. Let the solution of $(H_0+P)\psi=U\psi$ be $\psi=\psi_0+\psi_1+\psi_2$ where ψ_0 is the zeroth approximation, ψ_1, the first, and ψ_2 the second approximation to the correct wave function.

Then $-f_\lambda=\int\psi_0^2\frac{\partial V_0}{\partial\lambda}d\tau$ zeroth approximation

$$+\left\{\int\psi_0^2\frac{\partial P}{\partial\lambda}+2\int\psi_0\psi_1\frac{\partial V_0}{\partial\lambda}\right\}\text{first approximation}$$

$$+\left\{2\int\psi_0\psi_1\frac{\partial P}{\partial\lambda}+2\int\psi_0\psi_2\frac{\partial V_0}{\partial\lambda}+\int\psi_1^2\frac{\partial V_0}{\partial\lambda}\right\}\text{second approximation}$$

It is seen that it will be very advantageous to choose the parameter λ such that $\frac{\partial V_0}{\partial \lambda} = 0$. If this is possible, then

$$-f_\lambda = \left\{ \int \psi_0^2 \frac{\partial P}{\partial \lambda} \, d\tau \right\} \quad \text{first approximation}$$

$$+ \left\{ 2 \int \psi_0 \psi_1 \frac{\partial P}{\partial \lambda} \, d\tau \right\} \quad (4) \quad \text{second approximation.}$$

But, by the usual perturbation methods,

$$\psi_0 = \phi_0 \quad , \qquad \psi_1 = \sum_K \frac{(0|P|K)}{E_0 - E_K} \phi_K ,$$

where ϕ_0 is the wave function of the system in the unperturbed normal state, of energy E_0 , and ϕ_K is that of the unperturbed system in state K, of energy E_K., and $(0|P|K) = \int \phi_0 P \phi_K \, d\tau$.

Substituting this in (4) we obtain

$$-f_\lambda = \left(0 \left| \frac{\partial P}{\partial \lambda} \right| 0\right) + 2 \sum_K \frac{(0|P|K)(K|\frac{\partial P}{\partial \lambda}|0)}{E_0 - E_K} \qquad (5)$$

We can now make some applications of the equation (5) to van der Waals forces and polarizability.

4. VAN DER WAALS FORCES

We shall first consider the case of two atoms, because of its relative simplicity. Let, here as later, Greek subscripts $\alpha, \beta, \cdots$ stand for nuclei, and Roman ones i, j, k .. for electrons. If R is the separation of the two atoms then $P = \frac{1}{R^3} Q$ where $Q = \sum_{i,j} (x_i x_j + y_i y_j - 2 z_i z_j)$ summed over all electrons i of one atom, and all electrons j of the other atom.* Let our λ parameter be R; then since only the perturbation P involves R, we

*H. Margenau. Rev.Mod. Phys. 11, page 1 (1939)

can use equation (5). Assume the atoms have no permanent dipole moments, or $(o\,o|Q|o\,o)=0$ then (5) gives the relation,

$$f = -\frac{6}{R^7}\sum_{k,l}\frac{(o\,o|Q|k\,l)^2}{E_o+F_o-E_k-F_l}$$

using the quantum numbers, k, l

for the two different atoms, energies E_k and F_l.

For several atoms we take $P = \sum_{\alpha,\beta}\frac{1}{R_{\alpha\beta}}Q_{\alpha\beta}$

where $R_{\alpha\beta}$ is the distance from atom α, to atom β, and

$Q_{\alpha\beta} = \sum(xx+yy-2zz)$, summed for pairs of electrons of the atoms α,β alone. We take for our λ parameter the number μ_ρ giving the displacement of nucleus ρ in some direction. Our force f_{μ_ρ} is force on ρ in the direction of μ_ρ. The non vanishing terms, if we assume no permanent dipoles, lead to

$$f_{\mu_\rho} = -6\sum_{\substack{\alpha\\ \text{EXCEPT }\rho}}\frac{\partial R_{\rho\alpha}}{\partial\mu_\rho}\cdot\frac{1}{R_{\alpha\rho}^7}\sum_{k_\rho,k_\alpha}\frac{(o\,o|Q|k_\alpha,k_\rho)^2}{E_{o_\alpha}+E_{o_\rho}-E_{k_\alpha}-E_{k_\rho}}$$

where k_γ are quantum numbers representing the various (orthogonal) states of atom γ of energy E_{k_γ}.

In words, the force on nucleus ρ in the μ_ρ direction is the sum for all other nuclei α, of the usual expression of van der Waals force that would exist between α and ρ, times the cosine of the angle between $R_{\rho\alpha}$ and the direction μ_ρ (ie. $\frac{\partial R_{\rho\alpha}}{\partial\mu_\rho}$).

This proves the well known result that to this degree of approximation van der Waals forces are inverse

7 power, central and additive forces.

5. POLARIZABILITY

The polarizability α is defined so that if E be the electric field an atom finds itself in, $M = \alpha E$ is the dipole strength induced. We are going to measure forces. The force on an atom with dipole strength M is $M \cdot \frac{\partial E}{\partial z}$

Let a be the z coordinate of the nucleus. We want to take a as our parameter; varying it gives the force on the nucleus. The results will be calculated at $a = 0$ however. We can take the perturbing potential $P = (z-a)E + \frac{1}{2}F(z-a)^2$ so the force on the nucleus should be, neglecting F^2 relative to E, $E + (\alpha E)F$ since E is the direct attraction (nucleus considered with unit charge). Now,

$$\frac{\partial P}{\partial a}\Big|_{a=0} = E + Fz \quad ; \quad P_{at\ a=0} = zE + \frac{1}{2}Fz^2$$

Using (5) we obtain,

$$\text{Force} = \underset{\substack{\uparrow \\ \text{direct} \\ \text{attraction}}}{E} + F\underset{\uparrow}{(0|z|0)} + EF\underset{\uparrow}{\sum_K \frac{2(0|z|K)^2}{E_0 - E_K}}$$

permanent dipole — induced dipole

The permanent dipole moment $(0|z|0)$ always equals 0 for atoms. Since the force on the induced dipole should be $\propto EF$ we see that

$$\alpha = \sum_K \frac{2(0|z|K)^2}{E_0 - E_K}$$ the usual expression.

6. OTHER MODIFICATIONS OF THE FORCE EQUATIONS

We shall extend the force equation (2) to get an even clearer picture of what it means. Suppose, for example, the system for which ψ is the wave function contains several nuclei, and let the coordinates of one of these nuclei, α, be $x^\alpha, y^\alpha, z^\alpha$ or x^α_μ where $\mu = 1,2,3$ mean X,Y,Z. Suppose our λ parameter to be one of these coordinates, and the resultant force on the nucleus α in the μ direction will be given directly by,

$$f^\alpha_\mu = -\int \psi\psi \frac{\partial V}{\partial x^\alpha_\mu}\, d\tau \qquad \text{from (2).}$$

Now V is the interaction of all the nuclei with each other ($V_{\alpha\rho}$), of each nucleus with an electron ($V_{\rho i}$), and of each electron with every other (V_{ij}); or

$$V = \sum_{\alpha,\rho} V_{\alpha\rho} + \sum_{\rho,i} V_{\rho i} + \sum_{i,j} V_{ij}$$

The nuclear-nuclear forces are of no interest, since they are easy to calculate by Coulomb's law. We shall consider from here on only that part of the forces due to electrons.

Suppose x^i_μ are the coordinates of electron i, and, as before, X^α_μ those of nucleus α of charge q_α Then, $V_{\rho i} = \frac{q_\rho e}{R_{\rho i}}$ where $R^2_{\rho i} = \sum_{\mu=1}^{3} (X^\rho_\mu - x^i_\mu)^2$. So we see that

$$\frac{\partial V_{\rho i}}{\partial X^\alpha_\mu} = -\delta^\alpha_\rho \frac{\partial V_{\rho i}}{\partial x^i_\mu} \qquad \text{and that} \qquad \frac{\partial V_{ij}}{\partial X^\alpha_\mu} = 0$$

Then (2) leads to

$$f^\alpha_\mu = +\int \psi\psi' \sum_i \frac{\partial V_{\alpha i}}{\partial x^i_\mu}\, d\tau$$

$$= \int \sum_i \frac{\partial V_{\alpha i}}{\partial x^i_\mu} \left[\int \bar{\psi}\psi\, d\tau\right] d\tau \text{ since } \frac{\partial V_{\alpha i}}{\partial x^i_\mu} \text{ does not involve any}$$

electron coordinates except those of electron i.

Or finally

$$f_\mu^\alpha = \int [\sum_i \rho_i(x)] E_\mu^\alpha(x)\, dv \qquad (6)$$

where $E_\mu^\alpha = \frac{\partial V_{ii}}{\partial x_{i\mu}}$ is the field at the point x due to the nucleus α. The 3N space for N electrons has thus been reduced to a 3 space. This can be done since $E_\mu^\alpha(x^i)$ depends only on i and is the same function of x^i no matter which i we pick.

Thus the force on the nucleus is the attraction calculated electrostatically due to the charge distribution

$$\rho(x) = \sum_i \rho_i(x) \qquad \text{where} \quad \rho_i(x) = \int \frac{1}{2} \int \psi^* \psi \, dv' \qquad (7)$$

It is possible to simplify this further. Suppose we construct an electric field vector $\mathbb{F}$ (double letters $\mathbb{F}$ for vectors, corresponding single ones F_μ for their components) such that $\nabla \cdot \mathbb{F} = -4\pi \sum_i \rho_i(x)$; $\nabla \times \mathbb{F} = 0$ (8) or, for one electron, $\nabla \cdot \mathbb{F} = -4\pi \psi^2$. Now from the derivation of E_μ^α we know that it arises from the charge on nucleus α, say q_α, so that $\nabla \cdot E^\alpha = 0$ except at the charge q_α where its integral equals q_α.

Then, $$f_\mu^\alpha = -\frac{1}{4\pi} \int (\nabla \cdot F) E_\mu^\alpha \, dv = +\frac{1}{4\pi} \int F_\mu (\nabla \cdot E^\alpha)\, dv$$

$$= q_\alpha [F_\mu]_{at\ x^\alpha} \qquad (9),$$

the transformation of the integral being accomplished by integrating by parts. Or finally, the force on a nucleus is the charge on the nucleus times the electric field there due to all

the electrons.

This field is calculated classically from the charge distribution of each $\int i \int \psi\psi \, d\nu \, d\nu$.

For later purposes I will speak of a nuclear charge density ρ_N even tho the nuclear charges are concentrated ones. In this way, I can say for example,

$$\int_R \rho_N \mathbb{F} \, d\nu = \sum_{\substack{\alpha \\ \text{in } R}} q_\alpha \mathbb{F}_{\alpha x_\alpha} \qquad (10)$$

- is the force on all nuclei in the region R.

It is these forms of the theorem which are mentioned in the introduction as leading to the most easily interpretable results, as for example, the attractions arising from suitably placed charge concentrations.

7. THE CHARGE DISTRIBUTION FOR VAN DER WAALS FORCES*

We are now in a position to make an analysis of van der Waal's forces in the light of theorem (6). We shall only consider two atoms, α and β, each having one electron, 1 and 2. We wish to know what charge distribution nucleus α sees and how the attraction of α for this charge distribution leads to van der Waals force. All charges are considered to be unit charges. Proofs for the statements made in this paragraph have been relegated to an appendix.

Detailed calculation shows that the force on α due to the electron belonging to β is negligible (of order

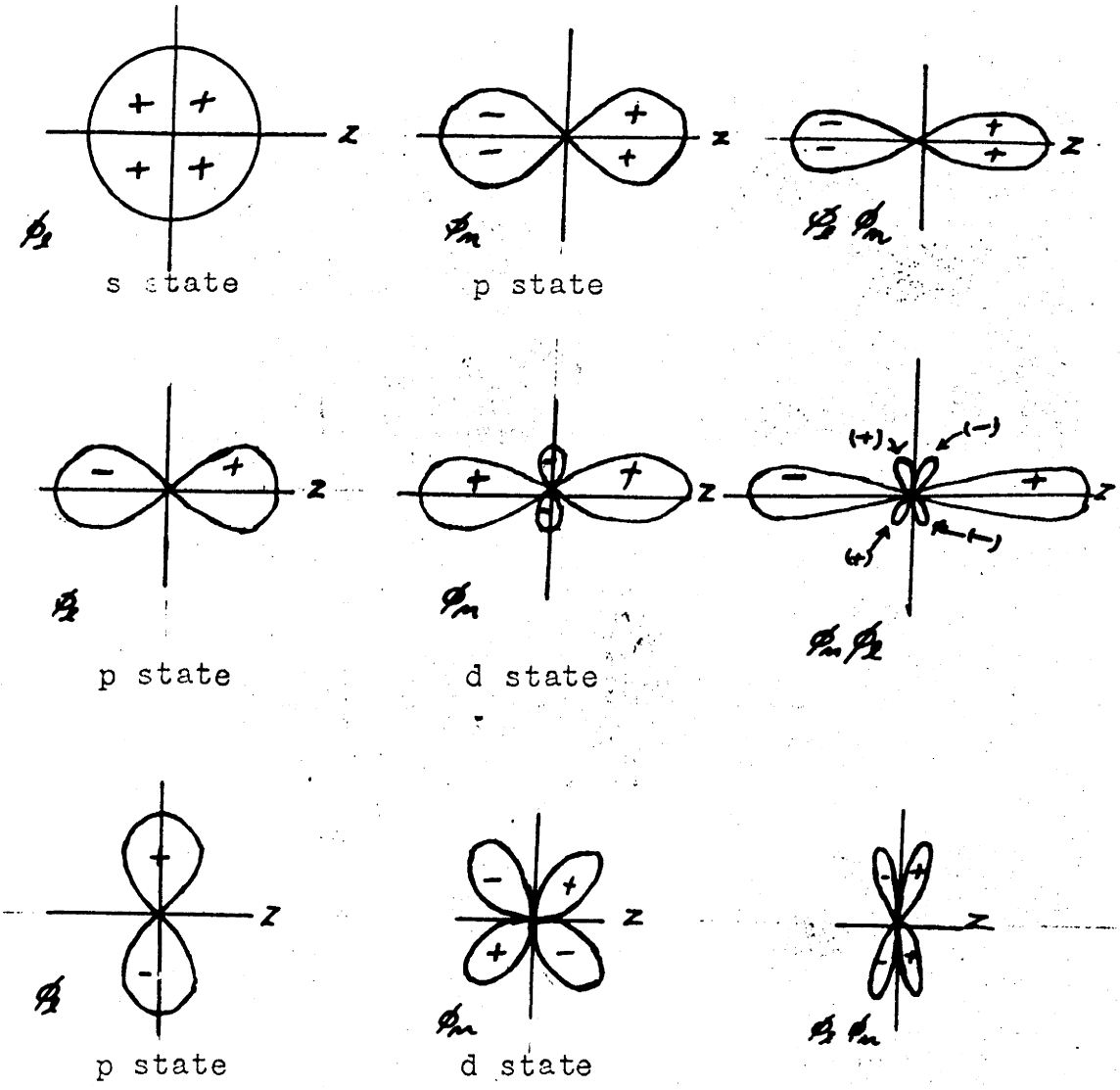
$\frac{1}{R^{10}}$) compared to that due to its own electron / (of order $\frac{1}{R^7}$). We thus need only find $\rho(1)$ or $\int\int \psi^2 d\tau_2$. The non-vanishing terms of this are either symmetrical about the nucleus, and hence leading to no force, or they are of the form $-\phi_\ell(1)\phi_m(1)$ where $(\ell|z|m) \neq 0$. If the ground state of α is an s state then, ℓ is an s state and m is a p state, or else ℓ is a p state and m is a d state. All these terms have positive coefficients if $(\ell|z|m)$ is positive, and negative coefficients if $(\ell|z|m)$ is negative. I have drawn some diagrams indicating the regions where these functions $\phi_m \phi_\ell$ are positive, or negative.

All these charge distributions are added together with suitable coefficients (positive for the terms in the diagrams), and added to the symmetrical distribution. The result is, of course, a distribution with a somewhat greater charge density on the right of the nucleus than on the left. Hence, the nucleus is urged to the right. Exact calculations of these terms lead, after several transformations, to the expression for the van der Waal's forces obtained before.

The charge distributions for some of the terms appear as below. These terms clearly give a dipole moment to the atom. They are added after multiplying by positive coefficients of order $\frac{1}{R^7}$ and so each atom has induced in it a dipole moment of this order. It is the

*See Also E. Wigner, Lectures on the Properties Of The Solid State

attraction of this nucleus for the unsymmetrical charge distribution that leads to the $\frac{1}{R^7}$ van der Waal's attraction.



The z direction is in the direction of the other nucleus, toward the right.

8. CONCLUDING REMARKS

I would suspect that the actual calculation of the forces in a real molecule to be not impractical. The

$\int \psi\psi^* \frac{\partial V}{\partial \lambda} d\tau$ is not too different from $\int \psi\psi^* V d\tau$, which latter must be calculated if the enrgy is to be known at all (as in the variational method).

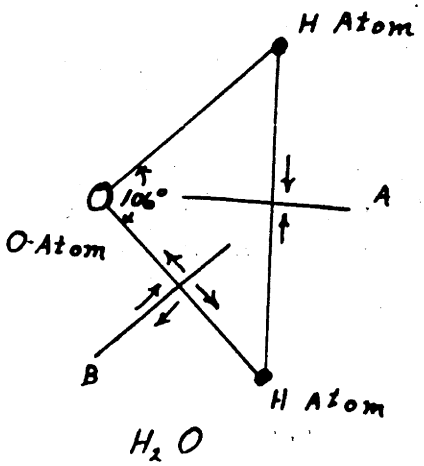
I have made an unsuccessful attempt to compare the accuracy of this method of getting the slope when we use an almost correct wave function obtained from the variational method to the accuracy of the ordinary way of getting the energy at successive points.

PART II.

9. STRESSES

In various molecular problems, questions arise as to the relative importance of certain of the forces. For example, how much of the tendency of H atoms in CH_4 to be tetrahedrally arranged arises from H-H repulsions, and how much to actual directive efforts of the carbon valence bonds. Similarly, is it the H-H repulsion which forces the H-O-H bonds to make an angle of 106 degrees, in spite of the tendency of the O valence bonds to issue at only 90 degrees. How strong is the H-H repulsive part so that we can get an idea of the oxygen bond "angular stiffness" in order to more accurately get elastic constants of such crystals as quartz.

A real answer to such problems could, of course, only come with considerations of the stresses in space in various regions near the molecule. For example, if the H-H repulsion is strong, large compression might be across plane A. Plane B might give tension coupled with shear, the tension to hold the H in, the shear arising from the strained state of the normally perpendicular O-H bonds.



H_2O

An answer to such questions can be given, of course, only if a stress tensor $S_{\mu\nu}$ can be found such that its integral over any closed surface R, $\int_R S_{\mu\nu} \cdot dS$ gives the resultant force on all nuclei inside R, + the time rate of change of the total momentum in that region R of the electrons (this last term vanishing in the steady state). Such a tensor for the "quantum field" would be just analogous to Maxwell's stress tensor for the elctromagnetic field.

10. FORM OF THE STRESS TENSOR FOR ONE ELECTRON.

We shall first consider the stresses in space for a system containing only one electron. The generalization from this is easy. Nuclei are considered held fixed.

We want $\int_R S_{\mu\nu} \cdot dS$ to be equal to the resultant force on all nuclei in R plus the time rate of change of the total momentum in R of the electron. This total momentum in R of the electron is just the integral over R of the electron momentum density. This last term vanishes in the steady state conditions, but we shall consider the general case. Now Green's theorem says that

$$\int_R S_{\mu\nu} \cdot dS = \int_R \nabla_\mu \cdot S_{\mu\nu} \, d\tau$$

By $\nabla_\mu \cdot S_{\mu\nu}$ is meant $\sum_{\mu=1}^{3} \frac{\partial S_{\mu\nu}}{\partial x_\mu}$

Thus we would like the following relation to hold:

$$\int_R \nabla_\mu \cdot S_{\mu\nu} \, d\tau = \int_R \rho_N F_\mu \, d\tau + \int_R \rho_N E_\mu \, d\tau + \frac{\partial}{\partial t}\left\{\int_R \left[\frac{h}{4\pi i}\left(\psi^* \frac{\partial \psi}{\partial x_\mu} - \psi \frac{\partial \psi^*}{\partial x_\mu}\right)\right] d\tau\right\}$$

or

$$\nabla_\mu \cdot S_{\mu\nu} = \rho_N F_\mu + \rho_N E_\mu + \frac{\partial}{\partial t}\left\{\frac{h}{4\pi i}\left[\psi^* \frac{\partial \psi}{\partial x_\mu} - \psi \frac{\partial \psi^*}{\partial x_\mu}\right]\right\}$$

where ρ_N = nuclear charge density, $\mathbf{E}$ the electric field due to nuclei, such that $\nabla \cdot \mathbf{E} = \rho_N$; $\nabla \times \mathbf{E} = 0$; $\mathbf{E} = \nabla V$ (12) and V is the potential the electron finds itself in. Also $\mathbf{F}$ equals the field due to the electron such that $\nabla \cdot \mathbf{F} = -4\pi\psi\psi^*$; $\nabla \times \mathbf{F} = 0$ (8) letting ψ be the wave function describing the state of the electron.

The first term on the right hand side of (11) is by (10) the force on the nuclei of R due to electrons, the second term the force due to other nuclei, and the third term is just the time rate of change of electron momentum.

It is seen that in defining $S_{\mu\nu}$ a similar difficulty arises as in defining the force above. The $S_{\mu\nu}$ is defined only through its divergence, and this does not permit a unique solution. I will proceed to find one solution of (11), however, reserving, for later, remarks on its uniqueness.

A tensor satisfying (11) exists, and it is convenient to present it in three parts;

$$S_{\mu\nu} = E_{\mu\nu} + M_{\mu\nu} + N_{\mu\nu} \qquad (15)$$

In this expression $N_{\mu\nu}$ is defined by

$$4\pi N_{\mu\nu} = \frac{1}{2}\left[2E_\mu E_\nu - \mathbf{E}\cdot\mathbf{E}\,\delta_{\mu\nu}\right] \qquad (16)$$

and is just the Maxwell stress tensor, for the nuclear-nuclear forces, and which contributes the second term on the right of (11). It need not be considered further.

Also $E_{\mu\omega}$ is given by

$$4\pi E_{\mu\omega} = E_\mu F_\omega + F_\mu E_\omega - \mathbb{E}\cdot\mathbb{F}\,\delta_{\mu\omega} \qquad (17)$$

and $$M_{\mu\omega} = \frac{\hbar^2}{16\pi^2 m}\left[\psi^+\frac{\partial^2\psi}{\partial x_\mu \partial x_\omega} + \psi\frac{\partial^2\psi^+}{\partial x_\mu \partial x_\omega} - \frac{\partial\psi^+}{\partial x_\mu}\frac{\partial\psi}{\partial x_\omega} - \frac{\partial\psi}{\partial x_\mu}\frac{\partial\psi^+}{\partial x_\omega}\right] \qquad (18)$$

We now prove that the divergence of these last two tensors gives the first and third terms on the right of (11).

11. PROOF OF THE STRESS TENSOR EQUATION

First we find

$$\nabla_\mu \cdot M_{\mu\omega} = \frac{\hbar}{4\pi i}\frac{\partial}{\partial t}\left[\psi^+\frac{\partial\psi}{\partial x_\omega} - \psi\frac{\partial\psi^+}{\partial x_\omega}\right] + \psi\psi^+\frac{\partial V}{\partial x_\omega} \qquad (19)$$

Proof. From (18)

$$2\nabla_\mu \cdot M_{\mu\omega} = \sum_{\mu=1}^{3}\frac{\hbar^2}{8\pi^2 m}\left\{\frac{\partial}{\partial x_\mu}\left[\psi^+\frac{\partial^2\psi}{\partial x_\omega \partial x_\mu} + \psi\frac{\partial^2\psi^+}{\partial x_\omega \partial x_\mu} - \frac{\partial\psi^+}{\partial x_\omega}\frac{\partial\psi}{\partial x_\mu} - \frac{\partial\psi}{\partial x_\omega}\frac{\partial\psi^+}{\partial x_\mu}\right]\right\}$$

$$= \frac{\hbar^2}{8\pi^2 m}\left\{\psi^+\frac{\partial}{\partial x_\mu}(\nabla^2\psi) + \psi\frac{\partial}{\partial x_\mu}(\nabla^2\psi^+) - (\nabla^2\psi^+)\frac{\partial\psi}{\partial x_\omega} - (\nabla^2\psi)\frac{\partial\psi^+}{\partial x_\omega}\right\}$$

But Schrodinger's equation says that

$$\frac{\hbar^2}{8\pi^2 m}\nabla^2\psi = \frac{\hbar}{2\pi i}\frac{\partial\psi}{\partial t} + V\psi \qquad \text{and} \qquad \frac{\hbar^2}{8\pi^2 m}\nabla^2\psi^+ = -\frac{\hbar}{2\pi i}\frac{\partial\psi^+}{\partial t} + V\psi^+$$

Substituting these values of $\nabla^2\psi$ and of $\nabla^2\psi^+$ in the above we get,

$$2(\nabla\cdot M_{\mu\omega}) = \frac{\hbar}{2\pi i}\psi^+\frac{\partial}{\partial x_\omega}\frac{\partial\psi}{\partial t} - \frac{\hbar}{2\pi i}\psi\frac{\partial}{\partial x_\omega}\frac{\partial\psi^+}{\partial t} + \psi^+\frac{\partial}{\partial x_\omega}(V\psi) + \psi\frac{\partial}{\partial x_\omega}(V\psi^+)$$

$$- \frac{\hbar}{2\pi i}\frac{\partial\psi^+}{\partial x_\omega}\frac{\partial\psi}{\partial t} + \frac{\hbar}{2\pi i}\frac{\partial\psi}{\partial x_\omega}\frac{\partial\psi^+}{\partial t} - V\psi^+\frac{\partial\psi}{\partial x_\omega} - V\psi\frac{\partial\psi^+}{\partial x_\omega}$$

$$= \frac{\hbar}{2\pi i}\frac{\partial}{\partial t}\left[\psi^+\frac{\partial\psi}{\partial x_\omega} - \psi\frac{\partial\psi^+}{\partial x_\omega}\right] + 2\psi\psi^+\frac{\partial V}{\partial x_\omega}$$ leading to (19).

Second we find $\nabla_\mu \cdot E_{\mu\nu} = \rho_N F_\nu - \psi\psi^* \frac{\partial V}{\partial x_\nu}$ (21)

Proof. From (17)

$$4\pi \nabla_\mu \cdot E_{\mu\nu} = \frac{\partial}{\partial x_\mu}[E_\mu F_\nu + F_\mu E_\nu] - \frac{\partial}{\partial x_\mu}[E_\alpha F_\alpha \delta_{\mu\nu}]$$

$$= E_\nu(\nabla \times \mathbb{F}) + F_\nu(\nabla \times \mathbb{E}) + E_\nu(\nabla \cdot \mathbb{F}) + F_\nu(\nabla \cdot \mathbb{E})$$

or, $4\pi \nabla_\mu \cdot E_{\mu\nu} = 4\pi F_\nu \rho_N - 4\pi\psi\psi^* E_\nu$ by (12) and (14)

or $\nabla_\mu \cdot E_{\mu\nu} = F_\nu \rho_N - \frac{\partial V}{\partial x_\nu}\psi\psi^*$ since $\mathbb{E} = \nabla V$ from (12), proving (21).

Adding (19) and (21) we obtain

$$\nabla_\mu \cdot (E_{\mu\nu} + M_{\mu\nu}) = \rho_N F_\nu + \frac{h}{4\pi i}\frac{\partial}{\partial t}\left[\psi^* \frac{\partial \psi}{\partial x_\nu} - \psi \frac{\partial \psi^*}{\partial x_\nu}\right] \quad (22)$$

Thus the sum of the divergence of $E_{\mu\nu}$ and $M_{\mu\nu}$ gives the first and third terms on the right of (11). Also the divergence of $N_{\mu\nu}$ gives the second term. Hence (11) is true.

12. CASE OF SEVERAL ELECTRONS

The following formulas may be proven in an analogous manner to those of one electron:

$\int \sum_i [S^i_{\mu\nu}] \cdot dS$ is the resultant force on nuclei in R plus time rate of change of momentum in R of the electrons. (11')

$S^i_{\mu\nu} = E^i_{\mu\nu} + M^i_{\mu\nu}$ The nuclear part $N_{\mu\nu}$ being left over for only one integration.

$$4\pi E^i_{\mu\nu} = E_\mu F^i_\nu + F^i_\mu E_\nu - \mathbb{E} \cdot \mathbb{F}^i \delta_{\mu\nu} \quad (17')$$

$$\nabla \cdot \mathbb{F}^i = -4\pi \int \bar{s} \int \psi\psi^* \, dv \, dv \; ; \; \nabla \times \mathbb{F}^i = 0 \; ; \; \mathbb{E} = \nabla V ; \; E_\mu = \sum_\alpha \frac{\partial V_{\alpha i}}{\partial x_{\alpha\mu}}$$

$$M^i_{\mu\nu} = \int \bar{s} \int \left(\frac{h^2}{16\pi^2 m_i}\right)\left[\psi^* \frac{\partial^2}{\partial x^i_\mu \partial x^i_\nu}\psi + \psi \frac{\partial^2}{\partial x^i_\mu \partial x^i_\nu}\psi^* - \frac{\partial \psi^*}{\partial x^i_\nu}\frac{\partial \psi}{\partial x^i_\mu} - \frac{\partial \psi}{\partial x^i_\nu}\frac{\partial \psi^*}{\partial x^i_\mu}\right] dv \, dv \ldots \quad (18')$$

Methods exactly analogous to those used in deriving (11) and (21) show that,

$$\nabla_\mu^i S_{\mu\nu}^i = \rho_N F_\nu^i + \frac{\partial}{\partial t}\int\bar{s}\int \frac{h}{4\pi i}\left[\psi^*\frac{\partial}{\partial x_\mu^i}\psi - \psi\frac{\partial\psi^*}{\partial x_\mu^i}\right] d\tau\, d\bar{s} + \int\bar{s}\int \psi\psi^*\frac{\partial I}{\partial x_\mu^i}\, d\tau\, d\bar{s}$$

where I is the interaction potential $\sum_{ij} V_{ij}$ of the electrons with each other.

But $\sum_i \int\bar{s}\int \psi\psi^*\frac{\partial I}{\partial x_\mu^i}\, d\tau\, d\bar{s} = 0$ since $\sum_i \frac{\partial I}{\partial x_i} = 0$.

Thus the validity of equation (11') is established.

13. UNIQUENESS

As previously mentioned, unfortunately $S_{\mu\nu}$ is not unique, and I can see no way of making it so. It is possible to add to it any tensor $A_{\mu\nu}$ whose divergence vanishes identically, since $S_{\mu\nu}$ is defined only through its divergence. Such divergenceless tensors are easy to construct. For example, if A is any vector and if

$$A_{\mu\nu} = \frac{\partial A_\mu}{\partial x_\nu} - \delta_{\mu\nu}(\nabla\cdot A) \qquad \text{then } \nabla_\nu \cdot A_{\mu\nu} \equiv 0$$

Of course $A_{\mu\nu}$ is symmetrical if $\nabla \times A = 0$

For example, with $A_\nu = \frac{1}{2}\frac{\partial}{\partial x_\nu}(\psi\psi^*)$ we find that we could have just as well written

$$M'_{\mu\nu} = M_{\mu\nu} - \frac{h^2}{8\pi^2 m}A_{\mu\nu} = \frac{h^2}{8\pi^2 m}\left[\psi^*\frac{\partial^2\psi}{\partial x_\mu \partial x_\nu} + \psi\frac{\partial^2\psi^*}{\partial x_\mu \partial x_\nu} - \frac{1}{2}\delta_{\mu\nu}\nabla^2(\psi\psi^*)\right]$$

This form of the tensor $M_{\mu\nu}$ might have been used instead of the form defined through equation (18). There is no reason to choose one rather than the other. The $M_{\mu\nu}$ of form (18) is the $T_{\mu\nu}$ mentioned by Pauli.* It is to

*Handbuch der Physik XXIV Page 106

be noticed that, although Pauli mentions space tensors for quantum mechanics he does not at all have the equivalent of our equation (11). The divergence of his $T_{\mu\nu}$ by (19), gives only the momentum flow part of the actual force, and this only after $-\frac{\partial V}{\partial x_\mu}\psi\psi$ is added to it.

It is to be noticed that we have considered the nuclei fixed. The generalization to the case when these are considered as moving also, is very simple to make. In that case we can take $-S_{\mu\nu}$ as the sum of $\sum_i M^i_{\mu\nu}$ as in the many electron case (18') except that some of the electrons are considered as nuclei. The tensors $E_{\mu\nu}$ and $N_{\mu\nu}$ are unnecessary. The $\int_R S_{\mu\nu}\,od\sigma = \int_R [\sum_i M^i_{\mu\nu}]\,od\sigma$ is then just the time rate of change of momentum contained in R due to electrons and to nuclei. In the steady state all this vanishes.

14. FORM FOR THE HYDROGEN ATOM

The stress tensor has been worked out for the space around a H atom in its normal state. I have used spherical coordinates $x_1 = r$, $x_2 = \theta$, $x_3 = \phi$. The wave function is $\psi = \sqrt{\alpha}\, e^{-\frac{\alpha}{2}r}$

We get

$$\frac{8\pi}{h^2} M^\mu_\nu = \begin{vmatrix} 0 & 0 & 0 \\ 0 & -\frac{\alpha^2}{2r} & 0 \\ 0 & 0 & -\frac{\alpha^2}{2r} \end{vmatrix} \cdot e^{-\alpha r}; \qquad \frac{8\pi}{h^2} E^\mu_\nu = \begin{vmatrix} \frac{\alpha}{r^2}+\frac{2}{r^3}+\frac{2}{\alpha r^4} & 0 & 0 \\ 0 & -\frac{\alpha}{r^2}-\frac{2}{r^3}-\frac{2}{\alpha r^4} & 0 \\ 0 & 0 & -\frac{\alpha}{r^2}-\frac{2}{r^3}-\frac{2}{\alpha r^4} \end{vmatrix} \cdot e^{-\alpha r}$$

So that,

$$\frac{8\pi^2}{h^2} S_{\omega}^{M} = e^{-\alpha N_a} \begin{vmatrix} \frac{\alpha}{R^2} + \frac{2}{R^3} + \frac{2}{\alpha R Y} & 0 & 0 \\ 0 & -\frac{\alpha^2}{2R} - \frac{\alpha}{R^2} - \frac{2\alpha}{\alpha R^3} - \frac{2}{\alpha R Y} & 0 \\ 0 & 0 & -\frac{\alpha^2}{2R} - \frac{\alpha}{R^2} - \frac{2}{R^3} - \frac{2}{\alpha R Y} \end{vmatrix} .$$

meaning, as one would expect, compression along r and tension transversely.

The largest values of $S_{\mu\nu}$ are near the origin and due almost entirely to $E_{\mu\nu}$, at large distances the values are small, but these are due primarily to $M_{\mu\nu}$.

15. CONCLUSION

Admittedly, this short account of the stress tensor leaves much to be desired. It would be very desirable to see just how the stress tensor behaves for a real molecule. Attempts have been made to calculate this out for the simple hydrogen molecular ion, but the formulas lead to integrals of considerable difficulty, when the calculation of $\mathcal{F}$ is attempted. Elliptical coordinates were used.

I would conclude that the actual calculation of the stress tensor for any real problem would be extremely difficult, although the information resulting from such a calculation may be well worth the trouble.

The major difficulty arises from the computation

of the field $\mathbb{F}$ due to the electron cloud. This could, in principle, be calculated using Green's theorem, if $\phi(P) = \int_{\infty} \frac{[\psi(q)]^2}{R_{Pq}} dV_q$ and $\mathbb{F} = \nabla\phi$ then $\nabla \cdot \mathbb{F} = -4\pi\psi^2$, but this is hardly a practical scheme.

APPENDIX

Proof of the statements made in paragraph 7.

Consider two nuclei α and β, with electrons 1 and 2 respectively. The perturbations due to the interactions is $\frac{1}{R^3}Q + \frac{1}{R^4}S$ where* $Q = [x_1x_2 + y_1y_2 - 2z_1z_2]$ (A)

$$S = \frac{3}{2}[(r_1^2 z_2 - z_1 r_2^2) + (2x_1x_2 + 2y_1y_2 - 3z_1z_2)(z_1 - z_2)] \quad (B)$$

We need only consider terms up to $\frac{1}{R^7}$ in the expansions as these will turn out to be the first which do not vanish. By the usual perturbation theory we set, $\psi = \psi_0 + \psi_1 + \psi_2$ where

$$\psi_0 = \phi_0(1)\,\phi_0(2)$$

$$\psi_1 = \frac{1}{R^3}\frac{(kl|Q|00)}{E_{00} - E_{kl}}\phi_k(1)\,\phi_l(2) + \frac{1}{R^4}\frac{(kl|S|00)}{E_{00} - E_{kl}}\phi_k(1)\,\phi_l(2)$$

$$\psi_2 = \frac{\frac{1}{R^6}(kl\,Q_{mn})(mn\,Q_{00}) + \frac{1}{R^7}(kl\,Q_{mn})(mn\,S_{00}) + \frac{1}{R^7}(kl\,S_{mn})(mn\,Q_{00})}{(E_{00} - E_{kl})(E_{00} - E_{mn})}\phi_k(1)\,\phi_l(2)$$

$$- \sigma\,\phi_0(1)\,\phi_0(2)$$

Where $-\sigma\phi_0\phi_0$ is needed for normalizing ψ. Summations are implied on k, l, m, n. E_{kl} means $E_k + E_l$ the energy of atom k + that of l.

The charge dehsity due to electron 1 is

$$\rho(1) = \int \psi^2 d\tau_2 = \int \psi_0^2 d\tau_2 + 2\int \psi_0\psi_1 d\tau_2 + 2\int \psi_0\psi_2 d\tau_2 + \int \psi_1\psi_1 d\tau_2$$

$$= (1 - 2\sigma)\phi_0(1)\phi_0(1) + 2\,\frac{\frac{1}{R^6}(ol\,Q_{mn})(mn\,Q_{00}) + \frac{1}{R^7}(ol\,Q_{mn})(mn\,S_{00}) + \frac{1}{R^7}(ol\,S_{mn})(mn\,Q_{00})}{(E_{00} - E_{ol})(E_{00} - E_{mn})}\phi_0\phi_l$$

$$+ \frac{1}{R^6}\frac{(kl\,Q_{00})(km\,Q_{00})}{(E_{00} - E_{kl})(E_{00} - E_{km})}\phi_l(1)\,\phi_m(1)$$

$$+ \frac{2}{R^6}\frac{(kl\,Q_{00})(km\,S_{00})}{(E_{00} - E_{kl})(E_{00} - E_{km})}\phi_l(1)\,\phi_m(1)$$

Since $ol\,Q_{00} = 0$ or $ol\,S_{00} = 0$.

* H. Margenau, Rev. Mod. Phys. 11. page 1, 1939.

Now let the subscript a represent the p state such that $(a|z|0) \neq 0$

Let α represent any p state at all.

Further let β represent the d state combining with α such that $(\alpha|z|\beta) \neq 0$

Notice that ${}_{k,l}Q_{00} = 0$ unless $k,l = \alpha_1, \alpha_2$, and ${}_{0\,k}Q_{\alpha_1\alpha_2} = 0$ unless $k = \beta_2$

${}_{\alpha_1\alpha_2}S_{k0} = 0$ unless $k = \alpha_1$, and ${}_{k\alpha_1}S_{\alpha_2 0} = 0$ unless $k = \beta_2$

and ${}_{\alpha k}S_{00} = 0$ unless $k = \beta$ because of (A) and (B).

The terms$^{(C)}$ may thus be simplified, the only remaining ones being,

$$\rho(1) = (1-2\theta)\phi_0\phi_0 + \frac{2}{R^4}\frac{(0\beta\,Q_{\alpha\alpha})(\alpha\alpha\,Q_{00})}{(E_{00}-E_{0\beta})(E_{00}-E_{\alpha\alpha})}\phi_0\phi_\beta + \frac{1}{R^4}\frac{\alpha\alpha\,Q_{00}\;\alpha\alpha\,Q_{00}}{(E_{00}-E_{\alpha\alpha})(E_{00}-E_{\alpha\alpha})}\phi_\alpha\phi_\alpha$$

$$+\frac{1}{R^7}\frac{(0\alpha\,Q_{\alpha\beta})(\alpha\beta\,S_{00})}{(E_{00}-E_{0\alpha})(E_{00}-E_{\alpha\beta})}\phi_0\phi_\alpha + \frac{2}{R^7}\frac{0\alpha\,S_{\alpha\alpha}\;\alpha\alpha\,Q_{00}}{(E_{00}-E_{\alpha\alpha})(E_{00}-E_{\alpha\alpha})}\phi_0\phi_\alpha$$

$$+\frac{2}{R^7}\frac{(\alpha\alpha\,Q_{00})(\alpha\beta\,S_{00})}{(E_{00}-E_{\alpha\alpha})(E_{00}-E_{\alpha\beta})}\phi_\alpha\phi_\beta$$

Summation is implied over all repeated suffixes of a given type. The terms in the first line are symmetrical, only the last three have an electric moment. A careful analysis of the possible coefficients of these terms leads to the result that the sign of the coefficient of $\phi_m\phi_l$ is the same as the sign of $(m|z|l)$. Hence the disymmetry of the various terms does not tend to cancel out, but rather to build up.

Now using equation (6) we see that to get the force on nucleus α we have two things to consider, the effect of electron 2 on α, and the effect on α, of its own electron, 1.

The first is $\int\left[\frac{z_2-R}{\sqrt{x_2^2+y_2^2+(z_2-R)^2}^3}\frac{1}{R^2}\right]\rho(1)\,d\tau_1$ where x_1, y_1, z_1 are the

coordinates of 2 relative to β , and R is the distance from α to β . This becomes, on expanding $\int \left(\frac{3Z_2}{R^3} + \frac{3}{2} \frac{2z_2^2 - x_2^2 - y_2^2}{R^4} \right) \rho(2)\, d\tau_2$

Now $\rho(1)$ is like $\rho(1)$ calculated above.

Thus the only term which can arise of order equal to or less than $\frac{1}{R^7}$ is $\int \phi_\beta \phi_\beta(1) \frac{z_2}{R^3} d\tau_2$ which clearly vanishes. As a matter of fact, the first non-vanishing terms are the $1/R^{10}$ terms. Thus the charge distribution around β only effects α as $1/R^{10}$.

The effect of the charge distribution 1 on nucleus α is, of course, $\int \rho(1) \frac{Z_1}{r_{1\alpha}} d\tau_1$ which becomes

$$F = \frac{2}{R^7} \frac{(\alpha\alpha\, Q_{\alpha\beta})(\alpha_\beta\, S_{\alpha\alpha})}{(E_{00} - E_{0\alpha})(E_{00} - E_{\alpha\beta})} \int \phi_0 \frac{Z_1}{r_{1\alpha}} \phi_\alpha\, d\tau_1 + \frac{2}{R^7} \frac{(\alpha\alpha\, S_{\alpha\alpha})(\alpha_\alpha\, Q_{00})}{(E_{00} - E_{0\alpha})(E_{00} - E_{\alpha\alpha})} \int \phi_0 \frac{Z_1}{r_{1\alpha}} \phi_\alpha\, d\tau_1$$

$$+ \frac{2}{R^7} \frac{\alpha\alpha\, Q_{00}\ \alpha\beta\, S_{00}}{(E_{00} - E_{\alpha\alpha})(E_{00} - E_{\alpha\beta})} \int \phi_\alpha \frac{Z_1}{r_{1\alpha}} \phi_\beta\, d\tau_1 \qquad (E)$$

These expressions (E) can be somewhat simplified by means of the relation $\int \phi_k \frac{z}{r^3} \phi_l\, d\tau = (E_l - E_k) \int \phi_k \frac{\partial \phi_l}{\partial z}\, d\tau$.

This may be proved by noting that $\int \phi_m \frac{\partial}{\partial z} \left(\frac{1}{r}\right) \phi_m = \int \phi_m \frac{\partial}{\partial z} \left(\frac{1}{r} \phi_m\right) - \int \phi_m \frac{1}{r} \frac{\partial \phi_m}{\partial z}$

But $H \phi_k = E_k \phi_k = (T + V) \phi_k = \left(T - \frac{1}{r}\right) \phi_k$ or $-\frac{1}{r} \phi_k = E_k \phi_k - T \phi_k$

from which it follows that, $-\frac{\partial}{\partial z} \left(\frac{1}{r} \phi_k\right) = E_k \frac{\partial \phi_k}{\partial z} - T \frac{\partial \phi_k}{\partial z}$

Substituting this we obtain

$$-\int \phi_m \frac{\partial}{\partial z} \left(\frac{1}{r}\right) \cdot \phi_m = E_m \int \phi_m \frac{\partial \phi_m}{\partial z} - \int \phi_m \left(T \frac{\partial \phi_m}{\partial z}\right) - \int E_m \phi_m \frac{\partial \phi_m}{\partial z} + \int (T \phi_m) \frac{\partial \phi_m}{\partial z}.$$

leading to the above relation since the terms in T cancel each other. Thus the expression (E) for force may be re-

duced to,

$$-F = 2\frac{(0\alpha\,Q_{\alpha\beta})(\alpha\beta\,S_{00})}{(E_{00}-E_{\alpha\beta})}\int\phi_\alpha\frac{\partial}{\partial z}\phi_0 + 2\frac{(0\alpha\,S_{\alpha\alpha})(\alpha\alpha\,Q_{00})}{(E_{00}-E_{\alpha\alpha})}\int\phi_\alpha\frac{\partial}{\partial z}\phi_0$$

$$+2\frac{(\alpha\alpha\,Q_{00})(\alpha\alpha\,S_{00})}{(E_{00}-E_{\alpha\alpha})(E_{00}-E_{\alpha\beta})}(E_\alpha-E_\beta)\int\phi_\alpha\frac{\partial}{\partial z}\phi_0. \qquad (F)$$

It might be desirous to prove this from the usual expression

$$F = 6\frac{(\alpha\alpha\,Q_{00})(\alpha\alpha\,Q_{00})}{E_{00}-E_{\alpha\alpha}}; \qquad (G)$$

but this is

$$2\frac{\alpha\alpha\,Q_{00}}{E_{00}-E_{\alpha\alpha}}\int\phi_\alpha(1)\phi_\alpha(1)\frac{\partial S}{\partial z_1}\phi_0(2)\phi_0(2)\,d\tau_1 d\tau_2 \text{ since } \frac{\partial S}{\partial z_1} = 3\varphi - (x_1^2+y_1^2-2z_1^2) \text{ from } (A)\text{ & }(B)$$

the last term, $(x_1^2+y_1^2-2z_1^2)$, vanishing on integration.

Now $\int\phi_\alpha\phi_\alpha\frac{\partial S}{\partial z_1}\phi_0\phi_0 = \int\phi_\alpha\phi_\alpha\frac{\partial}{\partial z_1}[S\phi_0\phi_0] - \int\phi_\alpha\phi_\alpha S\frac{\partial}{\partial z_1}(\phi_0\phi_0)$

But $S\phi_m\phi_n = (mn\,S_{kl})\phi_k\phi_l$

or $\int\phi_\alpha\phi_\alpha\frac{\partial S}{\partial z_1}\phi_0\phi_0 = -\alpha\alpha\,S_{00}\int\phi_k\phi_l\frac{\partial}{\partial z_1}(\phi_\alpha\phi_\alpha) - \alpha\alpha\,S_{mm}\int\phi_m\phi_m\frac{\partial}{\partial z_1}(\phi_0\phi_0)$

Considering only those terms which do not vanish, this becomes, after integrating over coordinates 2 on the right,

$$\int\phi_\alpha(1)\phi_\alpha(2)\frac{\partial S}{\partial z_1}\phi_0\phi_0 = -(\beta\alpha\,S_{00})\int\phi_\beta(1)\frac{\partial\phi_\alpha(1)}{\partial z_1}d\tau_1 - (\alpha\alpha\,S_{\alpha 0})\int\phi_\alpha\frac{\partial}{\partial z}\phi_0 \qquad (H)$$

Similarly

$$\int\phi_\beta\phi_\alpha\frac{\partial\varphi}{\partial z_1}\phi_0\phi_0 = -(\alpha\alpha\,Q_{00})\int\phi_\alpha\frac{\partial}{\partial z_1}\phi_\beta - (\beta\alpha\,Q_{\alpha 0})\int\phi_\alpha\frac{\partial}{\partial z_1}\phi_0 \qquad (I)$$

Since $\frac{\partial\varphi}{\partial z_1} = -2z_1$ this last expression (I) vanishes.

Now take $+2\frac{\alpha\alpha\,Q_{00}}{E_{00}-E_{\alpha\alpha}}\times(H) + 2\frac{\alpha\beta\,S_{00}}{E_{00}-E_{\alpha\beta}}\times(I)$.

The first part is F_λ by (G) and the second is 0 so we get,

$$F = -2\,(\alpha\kappa\,\Phi_{00})\,(\beta\kappa\,S_{00})\left(\frac{1}{E_{00}-E_{\alpha\beta}} - \frac{1}{E_{00}-E_{\alpha\alpha}}\right)\int \phi_\beta \frac{\partial}{\partial z_1}\phi_\alpha\, d\nu$$

$$-2\,\frac{(\alpha\kappa\,\Phi_{00})}{(E_{00}-E_{\alpha\alpha})}\,(\alpha\alpha\,S_{\alpha 0})\int \phi_\alpha \frac{\partial}{\partial z_1}\phi_0\, d\nu$$

$$-2\,\frac{(\beta\kappa\,\Phi_{\kappa 0})}{(E_{00}-E_{\alpha\beta})}\,(\alpha\beta\,S_{00})\int \phi_\alpha \frac{\partial}{\partial z}\phi_0\, d\nu \qquad \text{which is (F)}$$

Showing that (F) is equivalent to (G).