The Virial and Molecular Structure

J. C. Slater

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J. C. SLATER, *Massachusetts Institute of Technology*
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The virial theorem can be applied to a molecule, assuming that external forces are applied to keep the nuclei fixed. The mean electronic kinetic energy is then the negative of the mean total internal energy, plus a term arising from the virial of the external force. Since the external force is derivable from the knowledge of the total internal energy as function of nuclear position, this theorem gives a means of finding kinetic and potential energy separately for all configurations of the nuclei, as soon as the total energy is known, from experiment or theory. By using simple forms of curve for total energy, for the diatomic molecule, the kinetic and potential energy are derived and discussed. The curves give direct indication of the formation of the covalent bond, in cases where this occurs, by describing the removal of charge from the atoms to the region between the atoms, with resulting decrease of kinetic energy, increase of potential energy.

THE study of molecular structure has been too much based on particular models, rather than on general principles. One such general principle which has not been used and yet which seems capable of shedding considerable light on molecular problems, is the virial theorem. It is known that this theorem holds in quantum as in classical mechanics (see the Appendix for a simple proof) and its application to the theorem that the kinetic energy of an atom is the negative of the total energy is familiar. We shall use it, however, in a rather different way, applying it in the case where there are impressed forces.

THE VIRIAL THEOREM WITH IMPRESSED FORCES

The familiar statement of the virial theorem is

$$\overline{\text{K.E.}} = -\tfrac{1}{2}\overline{(xF_x + yF_y + \cdots)},$$

where the term on the right is a summation over all coordinates of the system, and F_x represents the force acting on the x coordinate, etc. We apply the theorem to a molecule consisting of electrons and nuclei attracting and repelling according to the inverse square law. Then, by a familiar argument, the virial $\overline{(xF_x + \cdots)}$ of the inverse square forces equals the potential energy of those forces, so that if the system is left to itself, the mean kinetic energy is minus half of the mean potential energy. But we shall not leave the system to itself. We shall rather assume that external forces of constraint act on the nuclei,

just sufficient to keep the nuclei at rest, instead of allowing them to vibrate as they would if they were free. In applying the virial theorem, we shall now have to compute merely the electronic kinetic energy, since there is no nuclear kinetic energy of vibration. The part of the virial coming from the inverse square forces will be, as usual, equal to the potential energy of these forces. But, in addition, there will be a contribution to the virial coming from the external forces of constraint. Thus the kinetic energy will, on the average, be different from minus a half of the mean potential energy. It will be equal to this quantity only in two cases: at infinite separation of all atoms from each other and at the equilibrium configuration, in which the atoms could exist without vibration at the absolute zero. For, in both these cases, the atoms would remain in equilibrium without external forces of constraint, these forces would have no virial and only the virial of the inverse square forces need be considered. This is true only to the extent to which we can neglect zero point vibration; it seems that the arguments of the present paper are all accurate only to that approximation, since it is not exactly legitimate to replace the coupling between electronic and nuclear motion by an external force acting on the nuclei.

To fix our attention on a definite problem, we shall consider a diatomic molecule, though the results we shall obtain can easily be generalized to any molecule or solid. Let the impressed force

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on nucleus 1 be F_1, on nucleus 2 F_2, where $F_2 = -F_1$, to keep the molecule as a whole in equilibrium. Then

$$\overline{(xF_x + \cdots)} = \overline{(r_1 \cdot F_1 + r_2 \cdot F_2)} = \overline{(r_2 - r_1) \cdot F_2}.$$

The vector $r_2 - r_1$ is simply the vector from the first nucleus to the second. Since F_2 is parallel to this vector, with a diatomic molecule, the result is $\overline{rF}$, where r is the internuclear distance, F the force to hold the nuclei in equilibrium. If the nuclei are attracting each other, this force is outward and the product is positive, while if they are repelling it is negative. Thus for a diatomic molecule in an attractive region, the mean kinetic energy is less than minus half the mean potential energy of the electrostatic forces, while in a repulsive region it is greater.

The Kinetic Energy of a Diatomic Molecule

Again, confining ourselves to the simple case of the diatomic molecule, we can easily see that the results of the last section allow an unambiguous determination of the mean electronic kinetic energy of the molecule as a function of internuclear distance, as soon as the curve of total electronic energy as function of distance (the familiar "potential energy curve" of the molecule) is known. Let this electronic energy, the sum of the electronic kinetic and potential energy $(T+V)$ be called E. Then the force exerted by the nucleus 2 is $-dE/dr$ and the force F which equilibrates this is dE/dr. Hence we have, dropping the average signs for convenience,

$$T = -\tfrac{1}{2}V - \tfrac{1}{2}r(dE/dr).$$

Solving this simultaneously with the equation $T + V = E$, we have

$$T = -E - r(dE/dr), \quad V = 2E + r(dE/dr).$$

These important equations determine the mean kinetic and potential energies as functions of r, one might almost say, experimentally, directly from the curves for E as function of r which can be found from band spectra. The theory is so simple and direct that one can accept the results without question, remembering only the limitation of accuracy mentioned above. Any model of molecular structure which permits the calcu-

lation of E will also permit the calculation of T and V directly from the model, without use of the virial theorem. These virial equations, then, will provide a valuable and independent check of the correctness of the wave functions of the model. This check in general is much more sensitive than that obtained from an approximately correct energy. For it is well known that the energy is stationary with respect to a slight variation of the wave function, so that almost the correct energy will be found from a poor wave function, whereas the relation between kinetic and potential energy changes rapidly for even small changes in wave function.

Kinetic and Potential Energy in Typical Cases

First we consider an attractive state of a molecule. At distances greater than the equilibrium distance, T is less than $-E$, going through a minimum in general, rising again, and equalling $-E$ at equilibrium. It is rising rapidly with decreasing distance at equilibrium. It does not continue to rise indefinitely, however. For as the nuclei of the two atoms are pushed into coincidence, the atoms coalesce into a single atom whose atomic number is the sum of the atomic numbers of the two atoms and, of course, this combined atom has a finite kinetic energy. This is in agreement with the result of the virial theorem. For, at very small distances, the total energy E will be the sum of two terms: the repulsion $Z_1 Z_2 e^2 / r$ of the two nuclei of atomic numbers Z_1 and Z_2, and the energy E' of the electrons of the combined atom. Thus for very small r's, we have

$$T = -(E' + Z_1 Z_2 e^2 / r)$$
$$-r(d/dr)(E' + Z_1 Z_2 e^2 / r) = -E',$$
$$V = 2(E' + Z_1 Z_2 e^2 / r) + r(d/dr)(E' + Z_1 Z_2 e^2 / r)$$
$$= 2E' + Z_1 Z_2 e^2 / r.$$

That is, the kinetic energy of the electrons is the negative of the total energy of the combined atom, a finite amount, while the potential energy is the sum of twice the total energy of the combined atom and the nuclear repulsion, all just as we should expect. For a repulsive state the situation is similar except that the preliminary

decrease of kinetic energy at large r is not present.

These results become more definite if we take some of the well-known approximate formulas for interatomic energy and compute kinetic and potential energy from them. We should state at the outset that no one of these formulas has the correct behavior at $r=0$. Hence we can expect a reasonable behavior only in the neighborhood of the equilibrium distance and for larger distances. First we take the power series formula used by Born and others for crystal structure. This gives

$$E = E_\infty - a/r^n + b/r^m,$$

$$T = -E_\infty - (n-1)a/r^n + (m-1)b/r^m,$$

$$V = 2E_\infty + (n-2)a/r^n - (m-2)b/r^m,$$

where E_∞ is the energy at infinite separation. Assuming that $m > n$, and that both m and n are greater than unity, we see that the kinetic energy first decreases with decreasing r, as we have stated, then goes through a minimum similar to that of the total energy, rising again and becoming infinite as $r=0$. The minimum of kinetic energy is easily shown to be at a larger r than the equilibrium distance, by a factor $\{(m-1)/(n-1)\}^{1/(m-n)}$, which, for example, is about 1.2 in the typical case $m=9$, $n=5$. Similarly, V rises for large r, goes through a maximum at a slightly larger r than the minimum of the kinetic energy, then decreases without limit. This, of course, neglects the fact which we have pointed out, that at still smaller distances the potential energy goes through a minimum and again increases, becoming positively infinite as r approaches zero. In Fig. 1 we show curves for E, T and V, for the case $m=9$, $n=5$. The case $n=1$, where the attractive forces are electrostatic, as in an ionic crystal or molecule, is exceptional. For in that case the second term in T, involving the factor $n-1$, is zero. The kinetic energy then does not go through its initial dip but begins to increase immediately as r decreases, going up with the same power of $1/r$ as the repulsive potential. The term $-a/r$, appearing in E, comes, in this case, entirely from the potential energy.

A purely repulsive state can be approximated, in terms of inverse powers, by a single term
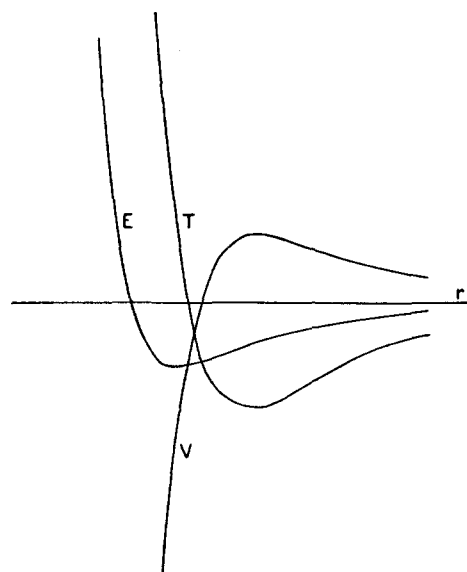

FIG. 1. Kinetic, potential and total energy of diatomic molecule as function of r. Energy is assumed to be of form $-a/r^5 + b/r^9$.

b/r^m, obtained in the formulas above by setting $a=0$. Here we see that the kinetic energy increases, and the potential energy decreases, with decreasing r, according to the same inverse power as the total energy. In this case again, the behavior for very small r is not correctly given. One interesting feature, which is met also in the attractive case, is that if m is large, the kinetic and potential energies separately are much larger than the total energy, which appears as the small difference of two large quantities.

The features of which we have spoken are not peculiar to the particular energy formula which we have used. If the energy is approximated by a sum of two exponential terms, as in the Morse curve, or in a repulsive case by a single exponential, the behavior in the neighborhood of the minimum and for large r is essentially similar to what we have described. The formulas are easily derived and it is hardly necessary to discuss them in detail.

INTERPRETATION OF KINETIC AND POTENTIAL ENERGY CURVES

The curves for kinetic and potential energy which we have discussed in the preceding section and plotted in Fig. 1, seem at first sight to be unexpected. We consider first the attractive case,

taking homopolar valence, for which n would be about 5 (or for which we would use a Morse curve, which gives results like Fig. 1). For we see that the decrease of energy which is responsible for binding seems to come from a decrease of kinetic energy, rather than of potential energy. The theory of homopolar binding suggests, on the other hand, that the mechanism of this binding is one in which charge concentrates between the nuclei and is attracted electrostatically by both nuclei, this attraction producing the binding. Thus we should expect that the binding would result from a decrease in potential energy, rather than kinetic. The answer to this paradox is not far to seek, however. We have just said that the first step in homopolar binding is the concentration of charge in the region between the nuclei. Now it requires a relatively small amount of energy (as we can see from the minimum principle for energy) to pull a certain amount of charge from the inner part of the atom, where it is ordinarily found, out to the periphery, as for example the region between the atoms. It can very well be that the decrease of potential energy made possible by this change, coming from the attraction of the electron of one atom by the nucleus of the other, can decrease the total energy enough to make this the stable configuration and produce binding. But when the charge is pulled out to the edge of the atom, its potential energy increases greatly, as it is separated from the nucleus, and its kinetic energy correspondingly decreases. Thus the rise of potential energy and the fall of kinetic energy, noticed in Fig. 1, are produced. As the atoms are pushed further together, however, a point is reached where the charge to be shared is fully removed to the region between the atoms. Further decrease of r then produces no further removal of charge to the periphery, no further decrease of kinetic and increase of potential energy. Instead, the other, more fundamental influences come into play. The kinetic energy begins to rise as the electrons are forced into smaller space. This may be likened to the adiabatic rise of energy of an electron gas compressed in a box. And the potential energy falls, as the negative charge concentrated between the atoms and the positive charge left over on the atoms come closer together. The

attractive force of the electrical attractions balances the repulsion of the electronic motion at equilibrium, the positive slope of the potential energy curve indicating large attraction, and the negative slope of the kinetic energy large repulsion. The curves show, then, that in the neighborhood of the equilibrium position, and even more at smaller distances, the behavior of the valence bond is rather simple and quite as we should expect. The peculiar behavior of potential and kinetic energies at larger r can be definitely associated with the formation of the shared electron pair which is responsible for the bond. This interpretation can be made rather unambiguously without use of models; for it is hard to see any meaning which can be given to an increase in electronic potential energy, decrease in kinetic, with much smaller change in total energy, other than a shift of electrons toward the outside of the atom.

Our identification of the minima and maxima, respectively, of the kinetic and potential energy for large r with the formation of a shared electron pair becomes much more reasonable when we consider the other cases of energy curves. We have already seen that these minima and maxima do not occur in the case where the attractive force is electrostatic, as in ionic molecules ($n = 1$), or in repulsive molecular states. In both these cases, the usual theory is that no electron pair is formed. The only action is the electronic repulsion when the atoms come closer together and, in the ionic case, the electrostatic attraction. This fits in perfectly with the behavior of the kinetic energy which rises rapidly, as the repulsive part of the energy does, at small distances.

The considerations which we have suggested indicate the importance of the virial in discussing molecular structure. There has been no attempt in this paper to deal exhaustively with its importance but only to point it out as a method which should be used in future work. And it should be recalled that it is as useful in treating more complicated molecules and solids, as with diatomic molecules. With a solid, for instance, if we subject it to a hydrostatic pressure p, the theorem becomes $T = -E + 3pv$, if the internal forces are electrostatic, as is well known. Thus, here, the kinetic energy is greater than $-E$ for

positive pressures, less for negative pressures and, in general, shows just the sort of behavior as function of volume that we have discussed for diatomic molecules as a function of r. The same conclusions regarding the nature of the inter-atomic forces can be drawn here as for molecules. Such conclusions were drawn before the wave mechanics by Schottky,[1] but his paper seems to have had but small influence in the theory of solids.

APPENDIX

Let Schrödinger's equation be

$$\sum_i -\frac{h^2}{8\pi^2 m_i}\frac{\partial^2 \psi}{\partial x_i{}^2}+(V-E)\psi = 0.$$

We differentiate with respect to x_j, and multiply by $x_j\bar{\psi}$, obtaining

$$\sum_i -\frac{h^2}{8\pi^2 m_i}x_j\bar{\psi}\frac{\partial^3 \psi}{\partial x_i{}^2\partial x_j}+\left(x_j\frac{\partial V}{\partial x_j}\right)\bar{\psi}\psi+x_j(V-E)\bar{\psi}\frac{\partial \psi}{\partial x_j}=0.$$

Now by Schrödinger's equation for $\bar{\psi}$, the last term is equal to

$$\sum_i \frac{h^2}{8\pi^2 m_i}x_j\frac{\partial^2 \bar{\psi}}{\partial x_i{}^2}\frac{\partial \psi}{\partial x_j}.$$

We substitute this term in and sum over x_j, obtaining

$$\sum_i -\frac{h^2}{8\pi^2 m_i}\sum_i\left[x_j\left(\bar{\psi}\frac{\partial^3 \psi}{\partial x_i{}^2\partial x_j}-\frac{\partial^2 \bar{\psi}}{\partial x_i{}^2}\frac{\partial \psi}{\partial x_j}\right)\right]+\left(\sum_i x_j\frac{\partial V}{\partial x_j}\right)\bar{\psi}\psi=0.$$

We now integrate this equation over the coordinate space. In doing this, we integrate the first term by parts. We do this by means of the identity

$$\sum_i x_j\left(\bar{\psi}\frac{\partial^3 \psi}{\partial x_i{}^2\partial x_j}-\frac{\partial^2 \bar{\psi}}{\partial x_i{}^2}\frac{\partial \psi}{\partial x_j}\right)=-2\bar{\psi}\frac{\partial^2 \psi}{\partial x_i{}^2}+\frac{\partial}{\partial x_i}\left[\bar{\psi}^2\frac{\partial}{\partial x_i}\left(\frac{\sum_i x_j(\partial \psi/\partial x_j)}{\bar{\psi}}\right)\right],$$

which can be proved, after a little manipulation, by performing the differentiations indicated on the right. In integrating the right side of this over the coordinates, the derivative integrates to zero if we assume the system to be a closed one, for then we take the limits of integration at infinity, where $\psi=0$. Hence we are left with only

$$\sum_i -\frac{h^2}{8\pi^2 m_i}\int \bar{\psi}\frac{\partial^2 \psi}{\partial x_i{}^2}d\tau=-\tfrac{1}{2}\int\sum_i x_j\left(\frac{-\partial V}{\partial x_j}\right)\bar{\psi}\psi\,d\tau.$$

The left side is recognized as the mean kinetic energy, the right side as $-\tfrac{1}{2}$ times the mean of $\sum_j x_j(-\partial V/\partial x_j)$, which is just the virial, when we remember that $F_j=-\partial V/\partial x_j$.

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[1] Schottky, Phys. Zeits. 21, 232 (1920).