AUGUST 15, 1939 PHYSICAL REVIEW VOLUME 56

Forces in Molecules

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(Received June 22, 1939)

Formulas have been developed to calculate the forces in a molecular system directly, rather than indirectly through the agency of energy. This permits an independent calculation of the slope of the curves of energy *vs.* position of the nuclei, and may thus increase the accuracy, or decrease the labor involved in the calculation of these curves. The force on a nucleus in an atomic system is shown to be just the classical electrostatic force that would be exerted on this nucleus by other nuclei and by the electrons' charge distribution. Qualitative implications of this are discussed.

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 tendency 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 is paramount.

Usually these problems have been considered through the agency of energy, and its changes with changing configuration 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 problem to be solved is the analysis of band spectra, strictly a problem of energy as such. It is the purpose of this paper to show that forces are almost as easy to calculate as energies are, and that the equations are quite as easy to interpret. In fact, all forces on atomic nuclei in a molecule can be considered as purely classical attractions involving Coulomb's law. The electron cloud distribution is prevented from collapsing by obeying Schrödinger's equation. In these considerations the nuclei are considered as mass points held fixed in position.

A usual method of calculating interatomic forces runs somewhat as follows.

For a given, fixed configuration 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 energy calculated. Proceeding in this way, a plot of energy *vs.* position is obtained. The force on a nucleus is of course the slope of this curve.

The following method is one designed to obtain the forces at a given configuration, when only the configuration is known. It does not require the calculations at neighboring configurations. That is, it permits a calculation of the slope of the energy curve as well as its value, for any particular configuration. It is to be emphasized that this allows a considerable saving of labor of calculations. To obtain force under the usual scheme the energy needs to be calculated for two or more different and neighboring configurations. Each point requires the calculation of the wave functions for the entire system. In this new method, only one configuration, the one in question, need have its wave functions computed in detail. Thus the labor is considerably reduced. Because it permits one to get an independent value of the slope of the energy curve, the method might increase the accuracy in the calculation of these curves, being especially helpful in locating the normal separation, or position of zero force.

In the following it is to be understood that the nuclei of the atoms in the molecule, or other atomic system, are to be held fixed in position, as point charges, and the force required to be applied to the nuclei to hold them is to be calculated. This will lead to two possible definitions of force in the nonsteady state, for then the energy is not a definite quantity, and the slope of the energy curve shares this indefiniteness. It will be shown that these two possible definitions are exactly equivalent in the steady-state case, and, of course, no ambiguity should arise there.

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 through $d\lambda$. This will define the force only when the molecule is in a steady state, of energy U, for then we can say $f_\lambda = -\partial U/\partial\lambda$. In the non-steady-state case we have no sure guide to a definition of force. For example, if $\bar{U} = \int \psi^* H \psi dv$ be the average energy of the system of wave function ψ and Hamiltonian H, we might define

$$f_\lambda' = -\partial(\bar{U})/\partial\lambda'. \tag{1}$$

Or again, we might take f_λ to be the average of $-\partial H/\partial\lambda$ or

$$f_\lambda = -\left\langle \frac{\partial H}{\partial\lambda} \right\rangle_{\text{Av}} = -\int \psi^* \frac{\partial H}{\partial\lambda} \psi dv. \tag{2}$$

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

Thus we shall prove, when $H\psi = U\psi$ and $\int \psi\psi^* dv = 1$ that,

$$\frac{\partial U}{\partial\lambda} = \int \psi^* \frac{\partial H}{\partial\lambda} \psi dv.$$

Now

$$U = \int \psi^* H \psi dv,$$

whence,

$$\frac{\partial U}{\partial\lambda} = \int \psi^* \frac{\partial H}{\partial\lambda} \psi dv + \int \frac{\partial\psi^*}{\partial\lambda} H\psi dv + \int \psi^* H \frac{\partial\psi}{\partial\lambda} dv.$$

Since H is a self-adjoint operator,

$$\int \psi^* H \frac{\partial\psi}{\partial\lambda} dv = \int \frac{\partial\psi}{\partial\lambda} H\psi^* dv.$$

But $H\psi = U\psi$ and $H\psi^* = U\psi^*$ so that we can write,

$$\frac{\partial U}{\partial\lambda} = \int \psi^* \frac{\partial H}{\partial\lambda} \psi dv + U \int \frac{\partial\psi^*}{\partial\lambda} \psi dv + U \int \frac{\partial\psi}{\partial\lambda} \psi^* dv.$$

These last two terms cancel each other since their sum is,

$$U \frac{\partial}{\partial\lambda} \int \psi^* \psi dv = U \frac{\partial}{\partial\lambda}(1) = 0.$$

Whence

$$\frac{\partial U}{\partial\lambda} = \int \psi^* \frac{\partial H}{\partial\lambda} \psi dv$$

in the steady state. This much is true, regardless of the nature of H, (whether for spin, or nuclear forces, etc.). In the special case of atomic systems when $H = T + V$ where T is the kinetic energy operator, and V the potential, since $\partial H/\partial\lambda = \partial V/\partial\lambda$ we can write

$$f_\lambda' = f_\lambda = -\frac{\partial U}{\partial\lambda} = -\int \psi^* \psi \frac{\partial V}{\partial\lambda} dv. \tag{3}$$

The actual calculation of forces in a real molecule by means of this theorem is not impractical. The $\int \psi^* \psi (\partial V/\partial\lambda) dv$ is not too different from $\int \psi^* \psi V dv$, which must be calculated if the energy is to be found at all in the variational method. Although the theorem (3) is the most practical for actual calculations, it can be modified to get a clearer qualitative 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^α, Y^α, Z^α or $X_\mu{}^\alpha$ where $\mu = 1, 2, 3$, mean X, Y, Z. If we take our λ parameter to be one of these coordinates, the resultant force on the nucleus α in the μ direction will be given directly by

$$f_\mu{}^\alpha = -\int \psi\psi^* (\partial V/\partial X_\mu{}^\alpha) dv$$

from (3).

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

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

Suppose $x_\mu{}^i$ are the coordinates of electron i, and as before $X_\mu{}^\alpha$ those of nucleus α of charge q_α. Then $V_{\beta i}=q_\beta e/R_{\beta i}$, where

$$R_{\beta i}{}^2=\sum_{\mu=1}^{3}(X_\mu{}^\beta-x_\mu{}^i)^2.$$

So we see that

$$\frac{\partial V_{\beta i}}{\partial X_\mu{}^\alpha}=-\delta_\beta{}^\alpha\frac{\partial V_{\beta i}}{\partial x_\mu{}^i} \quad \text{and that} \quad \frac{\partial V_{ij}}{\partial X_\mu{}^\alpha}=0.$$

Then (3) leads to

$$f_\mu{}^\alpha=+\int\psi\psi^*\sum_i\frac{\partial V_{\alpha i}}{\partial x_\mu{}^i}dv-\sum_\beta\int\frac{\partial V_{\alpha\beta}}{\partial X_\mu{}^\alpha}\psi\psi^* dv$$

$$=\int\sum_i\frac{\partial V_{\alpha i}}{\partial x_\mu{}^i}\left[\int i\int\psi\psi^*dv\right]dv-\sum_\beta\frac{\partial V_{\alpha\beta}}{\partial X_\mu{}^\alpha} \qquad (4)$$

since $\partial V_{\alpha i}/\partial x_\mu{}^i$ does not involve any electron coordinate except those of electron i. $\int i\int\cdots dv$ means the integral over the coordinates of all electrons except those of electron i. The last term has been reduced since $\partial V_{\alpha\beta}/\partial x_\mu{}^\alpha$ does not involve the electron coordinates, and is constant as far as integration over these coordinates goes. This term gives ordinary Coulomb electrostatic repulsion between the nuclei and need not be considered further. Now $e\int i\int\psi\psi^* dv$ is just the charge density distribution $\rho_i(x)$ due to electron i, where e is the charge on one electron. The electric field $E_\mu{}^\alpha(x^i)$ at any point x^i due to the nucleus α is $(1/e)\partial V_{\alpha i}/\partial x_\mu{}^i$, so that (4) may be written

$$f_\mu{}^\alpha=\int\left[\sum_i\rho_i(x)\right]E_\mu{}^\alpha(x)dv-\sum_\beta\frac{\partial V_{\alpha\beta}}{\partial X_\mu{}^\alpha}.$$

The $3N$ space for N electrons has been reduced to a 3 space. This can be done since $E_\mu{}^\alpha(x^i)$ depends only on x^i and is the same function of x^i no matter which i we pick. This implies the following conclusion:

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 the other nuclei and by the electron charge density distribution for all electrons,

$$\rho(x)=\sum_i\rho_i(x).$$

It is possible to simplify this still further. Suppose we construct an electric field vector F such that

$$\nabla\cdot F=-4\pi\rho(x)\,;\quad \nabla\times F=0.$$

Now from the derivation of $E_\mu{}^\alpha$ we know that it arises from the charge q_α on nucleus α, so that $\nabla\cdot E^\alpha=0$ except at the charge α where its integral equals q_α. Further,

$$-\sum_\beta\frac{\partial V_{\alpha\beta}}{\partial X_\mu{}^\alpha}=q_\alpha\left[\sum_\beta E_\mu{}^\beta\right]_{\text{at }x^\alpha}.$$

Then

$$f_\mu{}^\alpha=-\frac{1}{4\pi}\int(\nabla\cdot F)E_\mu{}^\alpha dv-\sum_\beta\frac{\partial V_{\alpha\beta}}{\partial x_\mu{}^\alpha}$$

$$=+\frac{1}{4\pi}\int F_\mu(\nabla\cdot E_\mu{}^\alpha)dv-\sum_\beta\frac{\partial V_{\alpha\beta}}{\partial x_\mu{}^\alpha}$$

$$=q_\alpha\left[F_\mu\right]_{\text{at }x^\alpha}+q_\alpha\left[\sum_\beta E_\mu{}^\beta\right]_{\text{at }x^\alpha} \qquad (5)$$

the transformation of the integral being accomplished by integrating by parts. Or finally, the force on a nucleus is the charge on that nucleus times the electric field there due to all the electrons, plus the fields from the other nuclei. This field is calculated classically from the charge distribution of each electron and from the nuclei.

It now becomes quite clear why the strongest and most important attractive 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 antisymmetrical wave function, because it must be zero exactly between the two H atoms, cannot concentrate charge between them. The symmetrical solution, however, can easily permit charge concentration between the nuclei, and hence it is only the solution which is symmetrical that leads to strong attraction, and the formation of a molecule, as is well known. It is clearly seen that concentrations of charge between atoms lead to strong attractive forces, and hence, are properly called valence bonds.

Van der Waals' forces can also be interpreted as arising from charge distributions with higher concentration between the nuclei. The Schrödinger perturbation theory for two interacting atoms at a separation R, large compared to the radii of the atoms, leads to the result that the charge distribution of each is distorted from central symmetry, a dipole moment of order $1/R^7$ being induced in each atom. The negative charge distribution of each atom has its center of gravity moved slightly toward the other. It is not the interaction of these dipoles which leads to van der Waals' force, but rather the attraction of each nucleus for the distorted charge distribution of its *own* electrons that gives the attractive $1/R^7$ force.

The author wishes to express his gratitude to Professor J. C. Slater who, by his advice and helpful suggestions, aided greatly in this work. He would also like to thank Dr. W. C. Herring for the latter's excellent criticisms.

AUGUST 15, 1939 PHYSICAL REVIEW VOLUME 56

Intercrystalline Thermal Currents as a Source of Internal Friction*

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(Received June 12, 1939)

An experiment has been designed to detect the contribution of intercrystalline thermal currents to the internal friction of polycrystalline metals. In accordance with a theory developed by one of the writers (C.Z.), the internal friction is a maximum when the vibration is partly isothermal and partly adiabatic with respect to adjacent grains. By passing in small steps from the nearly isothermal case of very small grain size through maximum internal friction to the nearly adiabatic case of large grain size, one can detect the relative importance of the intercrystalline thermal currents. Such an experiment has been performed on single phase 69–31 brass, with mean grain size ranging in small steps from 0.0006 cm to 0.4 cm, and with frequencies of 6000, 12,000 and 36,000 cycles per second. Not only was a maximum obtained with the anticipated grain size, but the maximum is of a larger order of magnitude than the background upon which it is superimposed. The internal friction in the extreme isothermal case ($Q>300{,}000$) was lower than has ever been observed for metals; in the extreme adiabatic case it approached the low values obtained for single crystals. This experiment indicates that in annealed nonferromagnetic metals at room temperature, intercrystalline thermal currents are the dominant cause of internal friction measured at small strains, aside from possible macroscopic thermal currents.

§1. Introduction

The term internal friction refers to the capacity of a solid to transform its ordered energy of vibration into disordered internal energy. One of the authors (C. Z.) has recently made a start at understanding the mechanism of this transformation.[1, 2, 3] His basic idea was that the direct coupling between the macroscopic and the internal coordinates may be treated by examining the thermoelastic effects which accompany vibration. Thus the increase in internal energy per cycle is equated to the temperature times the increase in entropy per cycle. The increase in entropy per cycle is obtained by studying the thermal currents which flow back and forth during vibration between stress inhomogeneities.

If these thermal currents are able nearly to maintain temperature equilibrium between the stress inhomogeneities, the vibration proceeds isothermally with little internal dissipation of energy. In the other extreme case of adiabatic vibration, the internal dissipation of energy is

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* This research was supported by a grant from the Penrose Fund of the American Philosophical Society, and by a grant from the Rumford Fund of the American Academy of Arts and Sciences.

[1] C. Zener, Phys. Rev. **52**, 230 (1937).

[2] C. Zener, Phys. Rev. **53**, 90 (1938).

[3] C. Zener, Proc. Phys. Soc. (in print).