The importance of the lattice softening to super-conductivity (via the electron-phonon interaction) will depend on how much of the phonon spectrum experiences the softening which we have detected in the megacycle range. A consideration of transport and equilibrium properties has indicated that for the high-frequency phonons some softening may occur, but it is probably of smaller magnitude than that found for the ultrasonic waves. However, an appreciable influence on superconductivity of the unusual phonon behavior may not require that the softening extend out to Debye frequencies. Morin and Maita[5] have found from specific-heat data that for the high-T_c superconductors the important phonon frequencies involved in the super-conductivity are at least an order of magnitude smaller than the Debye frequency.

Finally, there is little evidence from existing data that the structural transformation has led to an appreciable reduction in the transition temperature for super-conductivity. For materials which do transform, the cubic state at 21°K clearly cannot possess any properties sufficiently superior for superconductivity to raise T_c by more than 4°K. Stress experiments[6,26] which have produced tetragonal strains comparable to what occur in the structural transformation do not alter T_c by more than 0.5°K. Since the difference in T_c between transforming and nontransforming samples is generally less than 0.5°K and apparently not consistent in sign, the effect of the structural transformation on T_c is small. However, the proposed fine structure in $n(\epsilon)$ is of the order $\sim kT_c$, and it is not evident what value (or average) of $n(\epsilon)$ determines T_c. A degradation of the super-conducting behavior could be present if such fine structure should limit T_c because of the width of the peak.

ACKNOWLEDGMENTS

Virial Theorem for the Homogeneous Electron Gas

PETROS N. ARGYRES

Lincoln Laboratory,* Massachusetts Institute of Technology, Lexington, Massachusetts

(Received 3 August 1966)

A proof is presented of the virial theorem for the interacting electron gas in a uniform positive background with the boundary conditions used in actual calculations of the total energy.

INTRODUCTION

THE virial theorem for an interacting electron gas in a uniform background of positive charge, a simple model useful in the theory of solids, was written some time ago by March[1] in the form

$$2\bar{T} + \bar{V} = -r_s d\bar{E}/dr_s. \tag{1}$$

Here $\bar{T}$, $\bar{V}$, and $\bar{E}$ are, respectively, the average kinetic, potential, and total energies per particle for the system in its ground state and r_s is the radius of a sphere containing one electron, in units of the Bohr radius a_0 $=\hbar^2/me^2$, i.e., $(4\pi/3)r_s{}^3a_0{}^3=\Omega/N$, where Ω is the volume and N the number of electrons. In conjunction with $\bar{E} = \bar{T} + \bar{V}$, this relationship can give the average kinetic and potential energies separately, once $\bar{E}$ is known as a function of r_s. Explicitly we have

$$\bar{T} = -\bar{E} - r_s \frac{d}{dr_s} \bar{E} = -\frac{d}{dr_s}(r_s\bar{E}), \tag{2}$$

$$\bar{V} = 2\bar{E} + r_s \frac{d}{dr_s}\bar{E} = \frac{1}{r_s}\frac{d}{dr_s}(r_s{}^2\bar{E}). \tag{3}$$

These relations have been quite useful.[2]

However, no proof of (1) has been reported in the literature.

A relation similar to Eq. (1) was proved long ago by Slater[3] for the electronic energies of a diatomic molecule with the nuclei fixed away from their equilibrium positions. Different proofs of the Slater relation have since been given by various authors.[4] Also for the system of interacting particles in a box, a relation analogous to (1) was used by de Boer[5] and proved later with the method of scaling by Cottrell and Paterson,[6] who paid particular

* Operated with support from the U. S. Air Force.

[1] N. H. March, Phys. Rev. **110**, 604 (1958).

[2] See, e.g., W. J. Carr, Jr., R. A. Caldwell-Horsfall, and A. E. Fein, Phys. Rev. **124**, 747 (1961); W. J. Carr, Jr., and A. A. Maradudin, *ibid.* **133**, A371 (1964); L. Hedin, *ibid.* **139**, A796 (1965).

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

[4] See, e.g., Per-Olov Löwdin, J. Mol. Spectry. **3**, 46 (1959).

[5] J. de Boer, Physica **15**, 843 (1949).

[6] T. L. Cottrell and S. Paterson, Phil. Mag. **42**, 391 (1951).

attention to the boundary conditions and their contribution to the virial. None of these proofs justifies relation (1) for the system for which it was stated by March,[1] because of both the presence of the positive background charge and the different boundary conditions.

Below we present a proof of the virial theorem (1) for the electron gas in a uniform background of neutralizing charge, with the boundary conditions used in actual calculations of $\bar{E}(r_s)$.

PROOF OF THE VIRIAL THEOREM

The Hamiltonian of the N electrons and the positive charge spread uniformly over the volume Ω is

$$H = T + V = T + V_c + V_{eb} + V_b. \qquad (4)$$

Here T is the kinetic energy of the electrons,

$$T = \sum_i \frac{\mathbf{p}_i{}^2}{2m}, \qquad (5)$$

V_e their Coulomb interaction energy,

$$V_c = \frac{1}{2} \sum_{i \neq j} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|}, \qquad (6)$$

V_{eb} the electron-background interaction,

$$V_{eb} = (-e) \sum_i \int_\Omega d^3x \frac{\rho}{|\mathbf{r}_i - \mathbf{x}|}, \qquad (7)$$

with $\rho = eN/\Omega$ the uniform positive-charge density, and V_b the energy of the background, i.e.,

$$V_b = \frac{1}{2} \int_\Omega d^3x \int_\Omega d^3x' \frac{\rho^2}{|\mathbf{x} - \mathbf{x}'|}. \qquad (8)$$

In Eq. (4) we have put $V = V_c + V_{eb} + V_b$. In the following it proves convenient to keep the number of electrons N fixed and consider how these quantities vary with Ω, or, more conveniently, with r_s. We have

$$\Omega \propto r_s{}^3, \quad \rho \propto r_s{}^{-3}, \qquad (9)$$

as follows from the definitions of r_s and ρ.

We observe now that V_{eb} and V_b are functions of r_s. Furthermore, $V_{eb}(\mathbf{r}_1, \cdots, \mathbf{r}_N, r_s)$ is a homogeneous function of all its variables $(\mathbf{r}_1, \cdots, \mathbf{r}_N, r_s)$ of degree (-1), as can be seen from Eqs. (7) and (9) by a change of the variable of integration. The Euler theorem for homogeneous functions then gives

$$\left(\sum_i \mathbf{r}_i \cdot \frac{\partial}{\partial \mathbf{r}_i} + r_s \frac{\partial}{\partial r_s} \right) V_{eb} = -V_{eb}. \qquad (10)$$

Similarly, $V_b(r_s)$ is a homogeneous function of r_s of

degree (-1) and thus

$$r_s \frac{\partial V_b}{\partial r_s} = -V_b. \qquad (11)$$

Finally, $V_c(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ is a homogeneous function of $(\mathbf{r}_1, \cdots, \mathbf{r}_N)$ of degree (-1) and therefore

$$\sum_i \mathbf{r}_i \cdot \frac{\partial V_c}{\partial \mathbf{r}_i} = -V_c. \qquad (12)$$

Adding the last three equations, we can write for the total potential energy $V(\mathbf{r}_1, \cdots, \mathbf{r}_N, r_s)$ of Eq. (4)

$$\sum_i \mathbf{r}_i \cdot \frac{\partial V}{\partial \mathbf{r}_i} = -V - r_s \frac{\partial V}{\partial r_s}. \qquad (13)$$

The kinetic energy $T = T(\mathbf{p}_1, \cdots, \mathbf{p}_N)$ is a homogeneous function of all $\mathbf{p}$'s of degree 2 and thus

$$\sum_i \mathbf{p}_i \cdot \frac{\partial T}{\partial \mathbf{p}_i} = 2T. \qquad (14)$$

Note that relations (13) and (14) are valid also as operator equations, since the components of the $\mathbf{p}$'s and the $\mathbf{r}$'s commute separately.

From the virial theorem in classical mechanics,[7] we are led to consider in the quantum-mechanical case the operator that corresponds to the time derivative of the operator[8]

$$G = \sum_i \mathbf{r}_i \cdot \mathbf{p}_i, \qquad (15)$$

that is

$$\dot{G} \equiv (i\hbar)^{-1} [G, H], \qquad (16)$$

where $[\ ,\ ]$ denotes the commutator. We recall that the commutation rules for $\mathbf{r}_i$ and $\mathbf{p}_j$ give the operator identities $[\mathbf{r}_i, f(\mathbf{p}_1, \cdots, \mathbf{p}_N)] = i\hbar \partial f / \partial \mathbf{p}_i$, $[\mathbf{p}_i, f(\mathbf{r}_1, \cdots, \mathbf{r}_N)] = -i\hbar \partial f / \partial \mathbf{r}_i$. Using these we find simply

$$[G, T] = \sum_i [\mathbf{r}_i, T] \cdot \mathbf{p}_i = i\hbar \sum_i \mathbf{p}_i \cdot \frac{\partial T}{\partial \mathbf{p}_i} = i\hbar 2T, \qquad (17)$$

where the last equality follows from Eq. (14), and

$$[G, V] = \sum_i \mathbf{r}_i \cdot [\mathbf{p}_i, V]$$

$$= -i\hbar \sum_i \mathbf{r}_i \cdot \frac{\partial V}{\partial \mathbf{r}_i} = i\hbar \left(V + r_s \frac{\partial V}{\partial r_s} \right), \qquad (18)$$

where for the last equality the relation (13) was used.

[7] See, e.g., H. Goldstein, *Classical Mechanics* (Addison-Wesley Publishing Company, Inc., Reading, Massachusetts, 1957), p. 69.

[8] Note that G is not Hermitian. Introducing the Hermitian operator $\bar{G} = (G + G^\dagger)/2$ gives us nothing new, since $G^\dagger = \sum_i \mathbf{p}_i \cdot \mathbf{r}_i = G + 3Ni\hbar$ and thus $\bar{G} = G + (3/2)Ni\hbar$ differs from G by a constant that commutes with H.

Thus, we have, on account of the homogeneities of the kinetic and potential energy functions, the operator relation

$$(i\hbar)^{-1}[G,H] = 2T + V + r_s \frac{\partial V}{\partial r_s}. \qquad (19)$$

The last term in Eq. (19) can also be written as $r_s \partial H/\partial r_s$, since T is independent of r_s in our scheme of keeping N fixed.

We can now prove relation (1) by taking the expectation value of both members of Eq. (19) with respect to the ground state of the system. If we denote this state by the normalized wave function $\Psi(\mathbf{r}) = \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_N)$, we have

$$H\Psi(\mathbf{r}) = E\Psi(\mathbf{r}), \qquad (20)$$

where $E = \langle \Psi | H | \Psi \rangle = \langle H \rangle$ is the ground-state energy for the system.

Since different considerations are necessary for various boundary conditions on the ground-state wave function, we shall discuss a number of possible boundary conditions separately.

Free Boundary Conditions

If we impose on the electrons no constraints other than those of their mutual repulsion and their attraction to the positive background in volume Ω, we may take the wave function $\Psi(\mathbf{r})$ to vanish rapidly when any one of its arguments $\mathbf{r}_i \to \infty$. Such boundary conditions are often used in evaluating $E(r_s)$ for $r_s \gg 1$.

In such a case the expectation value of the left-hand side of Eq. (19) vanishes, i.e.,

$$\langle [G,H] \rangle = 0. \qquad (21)$$

This is seen by developing the commutator, making use of Eq. (20) and the fact that H is a Hermitian operator with respect to functions $\Psi(\mathbf{r})$ and $G\Psi(\mathbf{r}) = -i\hbar \sum_i \mathbf{r}_i \cdot \partial\Psi(\mathbf{r})/\partial\mathbf{r}_i$, due to the boundary conditions on $\Psi(\mathbf{r})$. We thus find from Eq. (19)

$$2\langle T \rangle + \langle V \rangle = -r_s \left\langle \frac{\partial V}{\partial r_s} \right\rangle. \qquad (22)$$

We can now relate $\langle \partial V/\partial r_s \rangle$ to $\partial E/\partial r_s$, by noting that all quantities in Eq. (20) depend parametrically on r_s. Differentiating Eq. (20) with respect to r_s and then taking its expectation value, we obtain, since $\partial H/\partial r_s = \partial V/\partial r_s$,

$$\frac{\partial E}{\partial r_s} = \left\langle \frac{\partial V}{\partial r_s} \right\rangle + \int \Psi^*(H - E)\frac{\partial \Psi}{\partial r_s} d\tau, \qquad (23)$$

the integration extending over all space for each electron. We again note that, for the boundary conditions under consideration here, H is Hermitian with respect to Ψ and $\partial\Psi/\partial r_s$. This makes the second term on the

right-hand side of Eq. (23) zero and thus

$$\left\langle \frac{\partial V}{\partial r_s} \right\rangle = \frac{dE}{dr_s}. \qquad (24)$$

This gives, in conjunction with Eq. (22),

$$2\langle T \rangle + \langle V \rangle = -r_s dE/dr_s. \qquad (25)$$

Denoting the average energies per particle by a bar, we obtain a proof of relation (1) by dividing Eq. (25) by N, since N is just a constant independent of r_s.

Note that identical arguments can be used to prove Slater's[3] analogous relation for a diatomic molecule. The only difference is that r_s is replaced by the internuclear distance; Eq. (13) is still valid, since V is obviously a homogeneous function of the electronic and nuclear coordinates of degree (-1). For a general system of electrons and fixed nuclei, Eq. (25) takes the form

$$2\langle T \rangle + \langle V \rangle = -\sum_n \mathbf{R}_n \cdot (\partial E/\partial \mathbf{R}_n), \qquad (26)$$

where $\mathbf{R}_n$ are the nuclear coordinates.

Periodic Boundary Conditions

One may object to the free boundary conditions for the homogeneous electron gas, for then the volume of the system is not well defined; only the smeared positive charge has a definite volume Ω, whereas the electrons extend throughout space. Furthermore, the usual evaluations of $E(r_s)$, especially for $r_s \ll 1$, are performed with periodic boundary conditions for $\Psi(\mathbf{r})$ on Ω. It is of importance, therefore, to investigate whether these constraints contribute anything to the virial of the system.

If, for convenience, volume Ω is assumed to be in the form of a cube of side $a (\propto r_s)$, the potential energy V is then usually taken to be not exactly as given by (6)–(8), but in the form

$$V = \frac{1}{2\Omega} \sum_{i \neq j} \sum_{q \neq 0} \frac{4\pi e^2}{q^2} \exp[i\mathbf{q} \cdot (\mathbf{r}_i - \mathbf{r}_j)], \qquad (27)$$

where $\mathbf{q} = (2\pi/a)\mathbf{n}$ with $\mathbf{n} = (n_1, n_2, n_3)$ being $\pm$ integers. Expression (27), however, again gives a homogeneous function of $(\mathbf{r}_1, \cdots, \mathbf{r}_N, r_s)$ of degree (-1). Thus, the operator equation (19) is still valid, since in deriving it use was made only of the homogeneous character of $V(\mathbf{r}, r_s)$ and not its specific form. The periodic boundary conditions on the wave function are now

$$\Psi(\mathbf{r}_1, \cdots, \mathbf{r}_i + \mathbf{a}, \cdots, \mathbf{r}_N; a)$$
$$= \Psi(\mathbf{r}_1, \cdots, \mathbf{r}_i, \cdots, \mathbf{r}_N; a), \qquad (28)$$

where $\mathbf{a}$ denotes translations of any one of the Cartesian components of $\mathbf{r}_i$ by the cube lengths, i.e., $\mathbf{a} = (a, a, a)$, and the last argument $a (\propto r_s)$ explicitly denotes the dependence of Ψ on the size of the cube.

We first note that Eq. (21) is no longer valid, since H is *not* Hermitian with respect to functions Ψ and $G\Psi$ for these boundary conditions, $G\Psi$ not being a periodic function. Instead we have

$$(i\hbar)^{-1}\langle[G,H]\rangle = \int_\Omega \Psi^*(H-E)\left(\sum_i \mathbf{r}_i\cdot\frac{\partial\Psi}{\partial\mathbf{r}_i}\right)d\tau, \quad (29)$$

the integration extending over the volume Ω for each electron. Similarly, Eq. (24) is not valid for periodic boundary conditions, because again H is not Hermitian with respect to functions Ψ and $\partial\Psi(\mathbf{r};r_s)/\partial r_s$, the latter not being a periodic function. That is, the integral in Eq. (23) does not vanish now, but instead we have

$$r_s\left\langle\frac{\partial V}{\partial r_s}\right\rangle = r_s\frac{dE}{dr_s} - \int_\Omega \Psi^*(H-E)a\frac{\partial\Psi}{\partial a}d\tau, \quad (30)$$

since clearly $r_s\partial\Psi/\partial r_s = a\partial\Psi/\partial a$. Combining Eqs. (30) and (29) with the expectation value of Eq. (19), we have

$$2\langle T\rangle + \langle V\rangle + r_s\frac{dE}{dr_s} = \int_\Omega \Psi^*(H-E)\Phi d\tau, \quad (31)$$

where

$$\Phi(\mathbf{r}_1,\cdots,\mathbf{r}_N;a) \equiv \left(\sum_j \mathbf{r}_j\cdot\frac{\partial}{\partial\mathbf{r}_j} + a\frac{\partial}{\partial a}\right)\Psi(\mathbf{r}_1,\cdots,\mathbf{r}_N;a). \quad (32)$$

We now note that Φ, defined by Eq. (32), has the full periodicity of Ψ, Eq. (28), i.e.,

$$\Phi(\mathbf{r},a) = \Phi(\mathbf{r}+\mathbf{a}_i, a), \quad (33)$$

where we have introduced the notation $(\mathbf{r},a) \equiv (\mathbf{r}_1,\cdots, \mathbf{r}_i,\cdots,\mathbf{r}_N;a)$ and $(\mathbf{r}+\mathbf{a}_i, a) \equiv (\mathbf{r}_1,\cdots, \mathbf{r}_i+\mathbf{a}, \cdots,\mathbf{r}_N;a)$. To prove this, we observe that partial differentiations of Eq. (28) give

$$\frac{\partial\Psi}{\partial\mathbf{r}_j}(\mathbf{r},a) = \frac{\partial\Psi}{\partial\mathbf{r}_j}(\mathbf{r}+\mathbf{a}_i, a), \quad (34)$$

for all j including $j=i$, and

$$a\frac{\partial\Psi}{\partial a}(\mathbf{r},a) = \left(\mathbf{a}\cdot\frac{\partial\Psi}{\partial\mathbf{r}_i} + a\frac{\partial\Psi}{\partial a}\right)(\mathbf{r}+\mathbf{a}_i, a). \quad (35)$$

The notation in Eqs. (34) and (35) is meant to indicate that the partial derivatives of $\Psi(\mathbf{r},a)$ are evaluated at the values of the arguments shown in the parentheses at the right. If we multiply (34) by $\mathbf{r}_j\cdot$, sum over all j, and add Eq. (35) to it, we get on the left-hand side $\Phi(\mathbf{r},a)$ and on the right-hand side $\Phi(\mathbf{r}+\mathbf{a}_i, a)$. This proves Eq. (33).

With respect to functions Ψ and Φ that satisfy the periodic boundary conditions (28) and (33), it is clear that H is a Hermitian operator in Eq. (31). This makes the right-hand side of Eq. (31) vanish. Dividing the resulting expression by N, we prove relation (1) for periodic boundary conditions.

Null Boundary Conditions

Although not of direct relevance to the actual calculations of $E(r_s)$, it is of some interest to point out that the virial theorem (1) is valid also when the electrons are kept within the volume Ω by an infinite potential wall. In such a case the boundary condition is $\Psi=0$ when any one $\mathbf{r}_i$ is on the surface bounding Ω. One can then prove[9] that Φ, given by Eq. (32), also vanishes on the bounding surface. H is then Hermitian with respect to such functions and the integral in Eq. (31) vanishes again. This proves relation (1) for these boundary conditions.

Carr[10] has given a different proof of (1) for these boundary conditions, using the scaling method of Ref. 6.

COMMENT

It is clear from the proof above that the virial theorem (1) is valid not only for the average values of the energies when the system is in the ground state, but also when it is in any one of its stationary states, provided the corresponding wave functions are subject to the same boundary conditions. It is thus also valid for the canonical ensemble averages of the energies.

ACKNOWLEDGMENTS

[9] See Appendix of Ref. 6.
[10] W. J. Carr, Jr. (private communication).