

## Self-Consistent Phonons and the Coupled Electron-Phonon System

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Keating's recent dielectric-screening theory of metallic and nonmetallic crystals is extended to anharmonic systems within the context of the lowest-order self-consistent phonon approximation.

### I. INTRODUCTION

IN a recent paper, Keating<sup>1</sup> employed many-body perturbation theory to provide a unified formulation of the lattice-vibration problem in metallic and nonmetallic crystals within the context of the harmonic approximation. This treatment expresses the phonon excitation spectrum exactly in terms of a properly defined dielectric-screening matrix for the dressed electrons, no assumption being made about adiabaticity. More recently, Pick, Cohen, and Martin<sup>2</sup> obtained similar, though less general,<sup>3</sup> results—again, within the context of the harmonic approximation. Since both of the above-mentioned treatments restrict themselves to the case of small atomic displacements; it is of interest to ask how these results might be generalized to highly anharmonic systems, especially in light of the fact that significant advances have been made in recent years in the treatment of such systems. We refer here to the so-called self-consistent phonon theories.<sup>4</sup> For those systems for which the interaction energy is expressible in terms of a well-defined effective interionic potential depending only on the instantaneous position of the ions, the application of these self-consistent techniques is straightforward. However, for a rigorous treatment of the coupled electron-phonon system, one must from the very beginning include the electronic degrees of freedom.

The present work extends Keating's results to include anharmonic contributions in the lowest-order self-consistent phonon approximation. The technique employed is a functional-derivative Green's-function approach analogous to that used by Baym<sup>5</sup> in his early work on the coupled electron-phonon system. In the Sec. II, we derive an expression for the phonon propagator in the lowest-order self-consistent phonon theory, arriving at a result which bears many similarities to Keating's expression for the harmonic phonon pro-

pagator. Crucial to the derivation of our result is the establishment of an equilibrium fluctuation theorem from which the sum rules of Keating and of Pick *et al.* follow as special cases.<sup>6</sup>

In order to avoid a proliferation of indices in what follows, we confine ourselves to the case of a monatomic lattice. The extension to more than one atom per unit cell is straightforward.

### II. THEORY

We begin with the total Hamiltonian of the system

$$H = H_E + H_L + H_{EL},$$

where

$$H_E = \frac{1}{2m} \int d^3r (\nabla\psi^\dagger(\mathbf{r}t)) \cdot (\nabla\psi(\mathbf{r}t)) \\ + \frac{1}{2} e^2 \int d^3r_1 d^3r_2 \psi^\dagger(\mathbf{r}_1t) \psi^\dagger(\mathbf{r}_2t) \\ \times |\mathbf{r}_1 - \mathbf{r}_2|^{-1} \psi(\mathbf{r}_2t) \psi(\mathbf{r}_1t), \quad (1)$$

$$H_L = \sum_l \frac{1}{2M} [\mathbf{P}_l(t)]^2 + \frac{1}{2} \sum_{l \neq l'} (Ze)^2 V(\mathbf{X}_l(t) - \mathbf{X}_{l'}(t)),$$

$$H_{EL} = -Ze^2 \sum_l \int d^3r \rho_e(\mathbf{r}t) \phi(\mathbf{r} - \mathbf{X}_l(t)).$$

All operators are in the Heisenberg representation.  $\psi(\mathbf{r}t)$  is the field operator for the electrons and  $\mathbf{X}_l(t)$ ,  $\mathbf{P}_l(t)$  are the position and momentum operators for the ion associated with lattice site  $l$ .  $\rho_e(\mathbf{r}t) \equiv \psi^\dagger(\mathbf{r}t)\psi(\mathbf{r}t)$  is the electron-density operator. Finally,  $V(\mathbf{X}_l - \mathbf{X}_{l'})$  represents the ion-ion interaction and  $\phi(\mathbf{r} - \mathbf{r}_l)$  is the effective interaction between an electron at  $\mathbf{r}$  and an ion core at  $l$ . The equations of motion for  $\psi(\mathbf{r}t)$ ,  $\mathbf{X}_l(t)$  are easily written.<sup>5</sup> Thus, we proceed immediately to the equations satisfied by the appropriate interaction-picture imagi-

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<sup>1</sup> P. N. Keating, Phys. Rev. **175**, 1171 (1968).

<sup>2</sup> Robert M. Pick, Morrel H. Cohen, and Richard M. Martin, Phys. Rev. (to be published).

<sup>3</sup> Less general in the sense that the inverse screening matrix of Pick, Cohen, and Martin does not include contributions arising from the renormalization of the electronic spectrum via phonon-exchange contributions and other interactions with the phonon field. Also, Pick *et al.* work within the adiabatic approximation.

<sup>4</sup> N. Boccara and G. Sarma, Physics **1**, 219 (1965); P. Choquard, *The Anharmonic Crystal* (W. A. Benjamin, Inc., New York, 1967); T. R. Koehler, Phys. Rev. Letters **17**, 89 (1966); H. Horner, Z. Physik **205**, 72 (1967).

<sup>5</sup> G. Baym, Ann. Phys. (N. Y.) **14**, 1 (1961).

<sup>6</sup> See Ref. 1, Eq. (17). When one imposes the condition of charge neutrality, the "acoustic" sum rule of Pick *et al.* follows from Keating's result.

nary-time Green's functions, defined as

$$G(\mathbf{r}t, \mathbf{r}'t') \equiv \frac{1}{i} \frac{\langle [S(\beta) \psi(\mathbf{r}t) \psi^\dagger(\mathbf{r}'t')]_+ \rangle}{\langle [S(\beta)]_+ \rangle},$$

$$d_i^\sigma(t) \equiv \frac{\langle [S(\beta) X_i^\sigma(t)]_+ \rangle}{\langle [S(\beta)]_+ \rangle},$$

$$d_{i\nu}^{\sigma\sigma'}(t, t') \equiv (-i) \left( \frac{\langle [S(\beta) X_i^\sigma(t) X_{\nu'}^{\sigma'}(t')]_+ \rangle}{\langle [S(\beta)]_+ \rangle} - d_i^\sigma(t) d_{\nu'}^{\sigma'}(t') \right).$$

Here  $[\dots]_+$  denotes the time-ordering operation in the imaginary time interval  $[0, -i\beta]$  and  $\langle \dots \rangle$  denotes an equilibrium ensemble average with respect to  $H$ . Further,

$$S(\beta) \equiv \exp \left[ -i \left( \int_0^{-i\beta} dt \sum_{i\sigma} X_i^\sigma(t) J_i^\sigma(t) + \int_0^{-i\beta} dt \int d^3r \rho(\mathbf{r}t) U(\mathbf{r}t) \right) \right],$$

where we have introduced the external fields  $J_i^\sigma(t)$ , and  $U(\mathbf{r}t)$ .

Note that the external scalar potential  $U(\mathbf{r}t)$  couples to the *total* charge density

$$\rho(\mathbf{r}t) \equiv \rho_e(\mathbf{r}t) + Z \sum_i \frac{\nabla^2}{4\pi} \phi(\mathbf{r} - \mathbf{X}_i(t)). \quad (3)$$

The equations of motion for  $G$ ,  $d_i^\sigma$ ,  $d_{i\nu}^{\sigma\sigma'}$  may be written symbolically as

$$[G_0^{-1}(1\bar{1}) - \tilde{U}(1\bar{1}) - \sum(1\bar{1})]G(\bar{1}\bar{1}') = \delta(1-1'),$$

$$D^{-1}(1\bar{1})d(\bar{1}) = J(1) + K(1), \quad (4)$$

$$[D^{-1}(1\bar{1}) - M(1\bar{1})]d(\bar{1}\bar{1}') = \delta(1-1').$$

In the above, we employed the summation convention for repeated indices. For electron coordinates, 1 stands for  $(\mathbf{r}_1, t_1)$  and for lattice coordinates, 1 stands for  $(\sigma_1, l_1, t_1)$ .  $\mathbf{r}$ -space integrations are taken over all space and time integrations extend from 0 to  $-i\beta$ . Further, we have defined

$$G_0^{-1}(11') \equiv \left( i \frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} \right) \delta(t_1 - t_1') \delta(\mathbf{r}_1 - \mathbf{r}_1'),$$

$$D^{-1}(11') \equiv -M \frac{\partial^2}{\partial t_1^2} \delta(t_1 - t_1') \delta_{l_1, l_1'},$$

$$\tilde{U}(11') = \left\{ U(1) + e^2 V_c(1\bar{1}) [-iG(\bar{1}\bar{1}^+)] + \frac{Z}{4\pi} \sum_i \langle \bar{\nabla}_1^2 \phi(\bar{\mathbf{r}}_1 - x_i(\bar{t}_1)) \rangle \right\} \delta(1-1'),$$

$$V_c(11') \equiv |\mathbf{r}_1 - \mathbf{r}_1'|^{-1} \delta(t_1 - t_1'),$$

$$\sum(1\bar{1})G(\bar{1}\bar{1}') \equiv ie^2 V_c(1\bar{1}) [\delta/\delta U(\bar{1})]G(11'),$$

$$M(1\bar{1})d(\bar{1}\bar{1}') \equiv [\delta/\delta J(1')]K(1).$$

Finally,

$$(2) \quad K_{i\nu}^{\sigma_1}(t_1) = (Ze)^2 \sum_{\nu' \neq i} \langle \langle [S(\beta) \nabla_{i\nu}^{\sigma_1} V(\mathbf{X}_{i\nu}(t_1) - \mathbf{X}_{\nu'}(t_1))]_+ \rangle \rangle - Ze^2 \int d^3r' \times \langle \langle [S(\beta) \rho_e(\mathbf{r}'t_1) \nabla_{i\nu}^{\sigma_1} \phi(\mathbf{r}' - \mathbf{X}_{i\nu}(t_1))]_+ \rangle \rangle + Z \int d^3r' U(\mathbf{r}'t_1) \times \langle \langle [S(\beta) \nabla_{i\nu}^{\sigma_1} \frac{\nabla'^2}{4\pi} \phi(\mathbf{r}' - \mathbf{X}_{i\nu}(t_1))]_+ \rangle \rangle, \quad (5)$$

and we have introduced the notation

$$\langle \langle [S(\beta) A(\mathbf{r}t)]_+ \rangle \rangle \quad \text{for} \quad \langle [S(\beta) A(\mathbf{r}t)]_+ \rangle / \langle [S(\beta)]_+ \rangle.$$

Our goal at this point is to calculate the phonon self-energy function  $M(11')$  in a low-order approximation which treats both the lattice and the electronic spectrum self-consistently, yet makes no assumption about the size of the atomic displacements. This is accomplished in two steps. First, we assume that in lowest-order one need keep only those correlations between electronic and lattice motion which serve to dress the electronic spectrum. Formally, this is the statement that

$$\langle \langle [S(\beta) \rho_e(\mathbf{r}t) \phi(\mathbf{r}' - \mathbf{X}_{\nu'}(t'))]_+ \rangle \rangle = \langle \langle [S(\beta) \rho_e(\mathbf{r}t)]_+ \rangle \rangle \langle \langle [S(\beta) \phi(\mathbf{r}' - \mathbf{X}_{\nu'}(t'))]_+ \rangle \rangle. \quad (6)$$

Secondly, we assume that in dealing with functionals of the lattice operators  $\mathbf{X}_i(t)$ , one may make an expansion in terms of semi-invariants,<sup>7</sup> keeping only terms up to second order in such an expansion. Thus, for example,

$$\langle \langle [S(\beta) \phi(\mathbf{r} - \mathbf{X}_i(t))]_+ \rangle \rangle \equiv \langle \langle [S(\beta) \exp(-\mathbf{X}_i(t) \cdot \nabla)]_+ \rangle \rangle \phi(\mathbf{r}) \cong \exp[-\mathbf{d}_i(t) \cdot \nabla + \frac{1}{2} i \sum_{\sigma\sigma'} d_{i\nu}^{\sigma\sigma'}(t, t) \nabla^\sigma \nabla^{\sigma'}] \phi(\mathbf{r}),$$

and

$$\langle \langle [S(\beta) V(\mathbf{X}_i(t) - \mathbf{X}_i'(t))]_+ \rangle \rangle \cong \lim_{\tau \rightarrow 0} \exp\{(\mathbf{d}_i(t) - \mathbf{d}_i'(t)) \cdot \nabla + \frac{1}{2} i \sum_{\sigma\sigma'} [d_{i\nu}^{\sigma\sigma'}(t, t) + d_{\nu\nu}^{\sigma\sigma'}(t, t) - 2d_{i\nu}^{\sigma\sigma'}(t, t)] \nabla^\sigma \nabla^{\sigma'}\} V(\mathbf{r}).$$

<sup>7</sup> H. Horner, Z. Physik 205, 72 (1967).

Employing (6) and (7) in (5) we find that

$$\begin{aligned} \frac{\delta}{\delta J_{\nu^{\sigma'}}(t')} K_{i^{\sigma}}(t) &= (Ze)^2 \sum_{\nu''(\neq i), \sigma''} \langle \langle [S(\beta) \nabla_{i^{\sigma}} \nabla_{i^{\sigma''}} V(\mathbf{X}_i(t) - \mathbf{X}_{\nu''}(t))]_{+} \rangle \rangle [d_{i\nu^{\sigma''\sigma'}}(t, t') - d_{\nu^{\sigma''\sigma'}}(t, t')] \\ &\quad - Ze^2 \int d^3r' \left\{ \langle \langle [S(\beta) \nabla_{i^{\sigma}} \phi(\mathbf{r}' - \mathbf{X}_i(t))]_{+} \rangle \rangle \frac{\delta}{\delta J_{\nu^{\sigma'}}(t')} \langle \langle [S(\beta) \rho_e(\mathbf{r}'t)]_{+} \rangle \rangle \right. \\ &\quad \left. + \langle \langle [S(\beta) \rho_e(\mathbf{r}'t)]_{+} \rangle \rangle \sum_{\sigma''} \langle \langle [S(\beta) \nabla_{i^{\sigma}} \nabla_{i^{\sigma''}} \phi(\mathbf{r}' - \mathbf{X}_i(t))]_{+} \rangle \rangle d_{i\nu^{\sigma''\sigma'}}(t, t') \right\} \\ &\quad + Z \int d^3r' U(\mathbf{r}'t) \sum_{\sigma''} \left\langle \left\langle \left[ S(\beta) \nabla_{i^{\sigma}} \nabla_{i^{\sigma''}} \left[ \frac{\nabla'^2}{4\pi} \phi(\mathbf{r}' - \mathbf{X}_i(t)) \right]_{+} \right] \right\rangle \right\rangle d_{i\nu^{\sigma''\sigma'}}(t, t'). \quad (8) \end{aligned}$$

Following Baym, we evaluate

$$[\delta/\delta J(2)] \langle \langle [S(\beta) \rho_e(1)]_{+} \rangle \rangle$$

as

$$V_e^{-1}(1\bar{1}) [\delta(\bar{1} - \bar{1}') - K(\bar{1}\bar{1}')] [\delta/\delta J(2)] \Phi(\bar{1}'), \quad (9)$$

where

$$\Phi(1) \equiv Z \sum_i \langle \langle [S(\beta) \phi(\mathbf{r}_1 - \mathbf{X}_i(t_1))]_{+} \rangle \rangle,$$

and

$$V_e^{-1}(11') \equiv -(\nabla_1^2/4\pi) \delta(\mathbf{r}_1 - \mathbf{r}_1') \delta(t_1 - t_1').$$

$K(11')$  is defined by the integral equation

$$K(11') = \delta(1 - 1') + e^2 V_e(1\bar{1})$$

$$\times \left( \frac{\delta}{\delta \tilde{U}(\bar{1}')} \langle \langle [S(\beta) \rho_e(\bar{1})]_{+} \rangle \rangle \right) K(\bar{1}'1'). \quad (10a)$$

This last is equivalent to

$$K(11') = \delta \tilde{U}_e(1)/\delta U(1'), \quad (10b)$$

where

$$\tilde{U}_e(1) \equiv U(1) + e^2 V_e(1\bar{1}) \langle \langle [S(\beta) \rho_e(\bar{1})]_{+} \rangle \rangle.$$

Thus, we have the alternative definition

$$K(11') = \delta(1 - 1') + e^2 V_e(1\bar{1})$$

$$\times \left( \frac{\delta}{\delta U(1')} \langle \langle [S(\beta) \rho_e(\bar{1})]_{+} \rangle \rangle \right), \quad (11a)$$

which, within the context of the approximation (6), reduces to

$$\begin{aligned} K(11') &= \delta(1 - 1') + e^2 V_e(1\bar{1})(-i) \\ &\quad \times [\langle \langle [S(\beta) \rho_e(\bar{1}) \rho_e(1')]_{+} \rangle \rangle \\ &\quad - \langle \langle [S(\beta) \rho_e(\bar{1})]_{+} \rangle \rangle \langle \langle [S(\beta) \rho_e(1')]_{+} \rangle \rangle]. \quad (11b) \end{aligned}$$

(10b) defines  $K(11')$  as the response of the electrons alone to a scalar field which couples to both the electrons and ions. With all external fields set equal to zero,  $K$  may be identified as the inverse screening matrix for the electron system. Furthermore, (11b) relates  $K$  to the equilibrium electron density-density correlation function.

We now employ the approximation (7) to explicitly carry out the functional differentiation in (9). Thus,

$$\begin{aligned} \frac{\delta}{\delta J_{i_2^{\sigma_2}}(t_2)} \langle \langle [S(\beta) \rho_e(\mathbf{r}_1 t_1)]_{+} \rangle \rangle &= \int d^3r' dt' \left( -\frac{\nabla_1^2}{4\pi} \right) [\delta(\mathbf{r}_1 - \mathbf{r}') \delta(t_1 - t') - K(\mathbf{r}_1 t_1, \mathbf{r}' t')] \\ &\quad \times Z \sum_{\nu^{\sigma'}} \langle \langle [S(\beta) \nabla_{\nu^{\sigma'}} \phi(\mathbf{r}' - \mathbf{X}_{\nu}(t'))]_{+} \rangle \rangle d_{\nu i_2^{\sigma_2}}(t', t_2). \quad (12) \end{aligned}$$

This last result, in conjunction with (8), provides us with sufficient information to construct  $M(1,1')$  in lowest order. Turning off the external fields and introducing the time-temperature Fourier-series expansion

$$M_{i\nu^{\sigma\sigma'}}(t-t') = \frac{1}{(-i\beta)} \sum_{\nu} e^{-iz_{\nu}(t-t')} M_{i\nu^{\sigma\sigma'}}(z_{\nu}), \quad z_{\nu} = \pi\nu/(-i\beta), \quad \nu = \text{even integer},$$

we find that

$$\begin{aligned} M_{i\nu^{\sigma\sigma'}}(z_{\nu}) &= (Ze)^2 (\delta_{i\nu} \sum_{\nu''} \langle \nabla_{i^{\sigma}} \nabla_{i^{\sigma''}} V(\mathbf{X}_i - \mathbf{X}_{\nu''}) \rangle - \langle \nabla_{i^{\sigma}} \nabla_{i^{\sigma'}} V(\mathbf{X}_i - \mathbf{X}_{\nu}) \rangle) \\ &\quad + Ze^2 \int d^3r' \langle \nabla^{\sigma} \rho_e(\mathbf{r}') \rangle \langle \nabla^{\sigma'} \phi(\mathbf{r}' - \mathbf{X}_i) \rangle \delta_{i\nu} - (Ze)^2 \int d^3r' d^3r'' \langle \nabla^{\sigma} \phi(\mathbf{r}' - \mathbf{X}_i) \rangle \\ &\quad \times \left( -\frac{\nabla'^2}{4\pi} \right) [\delta(\mathbf{r}' - \mathbf{r}'') - K(r', r'', z_{\nu})] \langle \nabla^{\sigma'} \phi(\mathbf{r}'' - \mathbf{X}_{\nu}) \rangle. \quad (13) \end{aligned}$$

$K(\mathbf{r}', \mathbf{r}'', z_\nu)$  is defined analogously to  $M_{ll'\sigma\sigma'}(z_\nu)$ . We may further rewrite (13) by introducing the equilibrium-fluctuation theorem established in the Appendix. Thus,

$$M_{ll'\sigma\sigma'}(z_\nu) = (Ze)^2 (\delta_{ll'} \sum_{l''} \langle \nabla_l^\sigma \nabla_{l''}^{\sigma'} V(\mathbf{X}_l - \mathbf{X}_{l''}) \rangle - \langle \nabla_l^\sigma \nabla_{l'}^{\sigma'} V(\mathbf{X}_l - \mathbf{X}_{l'}) \rangle) \\ + (Ze)^2 \left[ \delta_{ll'} \lim_{\omega \rightarrow 0} \int d^3 r' d^3 r'' \left( \sum_{l''} \langle \nabla^\sigma \phi(\mathbf{r}' - \mathbf{X}_{l''}) \rangle \right) \left( -\frac{\nabla'^2}{4\pi} \right) [\delta(\mathbf{r}' - \mathbf{r}'') - K(\mathbf{r}', \mathbf{r}'', \omega + i0^+)] \right. \\ \left. \times \langle \nabla^{\sigma'} \phi(\mathbf{r}'' - \mathbf{X}_{l'}) \rangle - \int d^3 r' d^3 r'' \langle \nabla^\sigma \phi(\mathbf{r}' - \mathbf{X}_l) \rangle \left( -\frac{\nabla'^2}{4\pi} \right) [\delta(\mathbf{r}' - \mathbf{r}'') - K(\mathbf{r}', \mathbf{r}'', z_\nu)] \langle \nabla^{\sigma'} \phi(\mathbf{r}'' - \mathbf{X}_{l'}) \rangle \right]. \quad (14)$$

As a consequence of our using the relation (A7) we see that the translational-invariance condition

$$\lim_{\omega \rightarrow 0} \sum_l M_{ll'\sigma\sigma'}(\omega + i0^+) = 0$$

is trivially satisfied.

### III. DISCUSSION

Result (14) for the phonon self-energy represents the lowest-order self-consistent phonon approximation for the coupled electron-phonon system. A complete self-consistent solution requires what we evaluate the "smeared" ionic charge density  $(Z/4\pi) \sum_l \langle \nabla^2 \phi(\mathbf{r} - \mathbf{X}_l) \rangle$  using (7) and then proceed to solve (4) for the electron Green's function. This last then permits the evaluation of the kernel in the integral Eq. (10a) for the inverse screening matrix. Actual numerical calculations prove to be difficult, even in lowest order, although some degree of success has been achieved in certain cases.<sup>8</sup>

We note two features of result (14). The bare Coulomb interaction between cores has been replaced by a "smeared" Coulomb interaction. Furthermore, the result of averaging the electron-phonon interaction  $\sum_l \phi(\mathbf{r} - \mathbf{X}_l)$  is to modulate the form factor  $\phi(\mathbf{q} + \mathbf{K})$  by a Debye-Waller-like factor in reciprocal space.

Finally, we point out that Keating's sum rule follows from the equilibrium fluctuation theorem (generalized to more than one atom per unit cell) established in the Appendix if we specialize to the harmonic approximation.

### APPENDIX

We consider the following equilibrium-ensemble average of the electron-density operator  $\rho_e(\mathbf{r})$ :

$$\langle \rho_e(\mathbf{r}) \rangle_u = \text{Tr}[e^{-\beta H(u)} \rho_e(\mathbf{r})] / \text{Tr}[e^{-\beta H(u)}], \quad (A1)$$

where

$$H(u) \equiv e^{-iuA} H e^{iuA} = H - iu[A, H] + O(u^2).$$

Here  $H$  is the Hamiltonian defined in (1), and  $e^{iuA}$  is a unitary transformation defined in terms of the as yet unspecified Hermitian operator  $A$ .  $u$  is an arbitrary real parameter. We expand (A1) to first order in  $u$ ,

obtaining

$$\langle \rho_e(\mathbf{r}) \rangle_u = \langle \rho_e(\mathbf{r}) \rangle - u \int_0^\beta d\lambda \left\langle e^{\lambda H} \left( \frac{\partial}{\partial u} H(u) \right) e^{-\lambda H} \right\rangle \\ \times [\rho_e(\mathbf{r}) - \langle \rho_e(\mathbf{r}) \rangle] + O(u^2). \quad (A2)$$

Also, however,

$$\langle \rho_e(\mathbf{r}) \rangle_u = \langle e^{iuA} \rho_e(\mathbf{r}) e^{-iuA} \rangle \\ = \langle \rho_e(\mathbf{r}) \rangle + iu \langle [A, \rho_e(\mathbf{r})] \rangle + O(u^2). \quad (A3)$$

Equating the coefficients of  $u$  in (A2) and (A3) yields the equilibrium fluctuation theorem

$$-i \langle [A, \rho_e(\mathbf{r})] \rangle = \int_0^\beta d\lambda \left\langle e^{\lambda H} \left[ \frac{\partial}{\partial u} H(u) \right] e^{-\lambda H} \right\rangle \\ \times e^{-\lambda H} [\rho_e(\mathbf{r}) - \langle \rho_e(\mathbf{r}) \rangle]. \quad (A4)$$

Equating higher powers of  $u$  in the expansions of (A2) and (A3) would yield higher-order fluctuation theorems.

Let us consider the particular case where  $A = \mathbf{P}$ , the total momentum operator for the system of electrons. The unitary transformation is then the finite translation operator  $e^{iu \cdot \mathbf{P}}$  and

$$H(\mathbf{u}) = H - \sum_l \int d^3 r' (Ze^2) [\rho_e(\mathbf{r}' + \mathbf{u}) - \rho_e(\mathbf{r}')] \phi(\mathbf{r}' - \mathbf{X}_l).$$

(A4) now yields the relation

$$\langle \nabla \rho_e(\mathbf{r}) \rangle = \int d^3 r' (Ze^2) \sum_l \int_0^\beta d\lambda \\ \times \{ \langle [\nabla' \phi(\mathbf{r}' - \mathbf{X}_l(-i\lambda))] \rho_e(\mathbf{r}', -i\lambda) \rho_e(\mathbf{r}) \rangle \\ - \langle \langle \nabla' \phi(\mathbf{r}' - \mathbf{X}_l) \rangle \rho_e(\mathbf{r}') \rangle \langle \rho_e(\mathbf{r}) \rangle \} \\ = \int d^3 r' (Ze^2) \sum_l \langle \nabla' \phi(\mathbf{r}' - \mathbf{X}_l) \rangle \\ \times \int_0^\beta d\lambda [\langle \rho_e(\mathbf{r}', -i\lambda) \rho_e(\mathbf{r}) \rangle \\ - \langle \rho_e(\mathbf{r}') \rangle \langle \rho_e(\mathbf{r}) \rangle]. \quad (A5)$$

<sup>8</sup> N. S. Gillis, Phys. Rev. Letters 22, 1251 (1969).

The last equality above follows from functionally differentiating the relation (6) with respect to  $U(r,t)$ . From (A5), it follows immediately that

$$\begin{aligned} & \int d^3r \langle \nabla \rho_e(\mathbf{r}) \rangle \langle \nabla \phi(\mathbf{r} - \mathbf{X}_i) \rangle \\ &= (Ze^2) \int d^3r d^3r' \langle \nabla \phi(\mathbf{r} - \mathbf{X}_i) \rangle \\ & \quad \times \int_0^\beta d\lambda [\langle \rho_e(\mathbf{r}', -i\lambda) \rho_e(\mathbf{r}) \rangle - \langle \rho_e(\mathbf{r}') \rangle \langle \rho_e(\mathbf{r}) \rangle] \\ & \quad \times \sum_{\nu'} \langle \nabla' \phi(\mathbf{r}' - \mathbf{X}_{\nu'}) \rangle, \end{aligned}$$

which may be further rewritten as

$$\begin{aligned} & \int d^3r \langle \nabla \rho_e(\mathbf{r}) \rangle \langle \nabla \phi(\mathbf{r} - \mathbf{X}_i) \rangle \\ &= -(Ze^2) \lim_{\omega \rightarrow 0} \int d^3r d^3r' \langle \nabla \phi(\mathbf{r} - \mathbf{X}_i) \rangle L(\mathbf{r}', \mathbf{r}, \omega + i0^+) \\ & \quad \times \sum_{\nu'} \langle \nabla' \phi(\mathbf{r}' - \mathbf{X}_{\nu'}) \rangle. \quad (\text{A6}) \end{aligned}$$

$L(\mathbf{r}, \mathbf{r}', z)$  is defined in terms of the time-ordered density-density correlation function as

$$\begin{aligned} & -i \{ \langle [\rho_e(\mathbf{r}t) \rho_e(\mathbf{r}'t')]_+ \rangle - \langle \rho_e(\mathbf{r}) \rangle \langle \rho_e(\mathbf{r}') \rangle \} \\ &= \frac{1}{(-i\beta)} \sum_{\nu} e^{-iz_{\nu}(t-t')} L(\mathbf{r}, \mathbf{r}', z_{\nu}). \end{aligned}$$

But from (11b), we have that

$$\left( -\frac{\nabla^2}{4\pi} \right) [K(\mathbf{r}, \mathbf{r}', z_{\nu}) - \delta(\mathbf{r} - \mathbf{r}')] = e^2 L(\mathbf{r}, \mathbf{r}', z_{\nu}).$$

Hence, (A6) finally becomes

$$\begin{aligned} & \int d^3r \langle \nabla \rho_e(\mathbf{r}) \rangle \langle \nabla \phi(\mathbf{r} - \mathbf{X}_i) \rangle \\ &= -Z \lim_{\omega \rightarrow 0} \int d^3r d^3r' \langle \nabla \phi(\mathbf{r} - \mathbf{X}_i) \rangle \\ & \quad \times \left( -\frac{\nabla'^2}{4\pi} \right) [K(\mathbf{r}', \mathbf{r}, \omega + i0^+) - \delta(\mathbf{r} - \mathbf{r}')] \\ & \quad \times \sum_{\nu'} \langle \nabla' \phi(\mathbf{r}' - \mathbf{X}_{\nu'}) \rangle. \quad (\text{A7}) \end{aligned}$$