

## Density functional theory of superconductivity

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### ABSTRACT

We outline a first-principles approach to superconductivity based on a generalized density functional theory that has recently been developed by the present author. Within the generalized density functional framework it can be shown that the atomic nuclei-electron system of an extended solid in its ground state is either a metal or an insulator as long as the Born-Oppenheimer (BO) approximation applies. Any conceivable interaction mechanism of purely electronic character (including interaction with plasmons, magnons, etc.) can never reduce the total energy of the system to below its BO value associated with metallic conductivity or insulating properties. Consequently, a superconducting state whose total energy must necessarily be below that of the metallic state cannot possibly occur within the BO approximation. Hence, in order to bring about superconductivity, electron-phonon interaction is definitely indispensable. We briefly report a generalized-density-functional-based derivation of the gap equation as being the general key element of a first-principles theory of superconductivity.

### § 1. INTRODUCTION

Over the past 35 years since the advent of a microscopic theory of superconductivity there has been mounting evidence that the mechanism governing this extraordinary behaviour of solids is generically non-relativistic and should hence be describable within the framework of an  $(N + N_n)$ -particle Schrödinger equation for the  $N$  electrons of the solid in question and its  $N_n$  nuclei. This should, of course, apply to high- $T_c$  superconductivity as well. Distinctly different from this rather elementary first-glance view, the pioneering paper by Bardeen, Cooper and Schrieffer (BCC) (1957) was based on a second quantization scheme starting with a Hamiltonian in the corresponding form. A conceptual foundation of this kind was much in the spirit of Fröhlich's conviction that superconductivity can appropriately be treated only within a field theoretical approach which he advanced in 1950 (Fröhlich, Pelzer and Zienau 1950). The ensuing work, most prominently that of Eliashberg (1960), and the entire literature that grew out of these pioneering theoretical studies followed consistently that school of thought. There has never been a successful off-stream attempt to tackle the superconductivity problem directly from the more elementary starting point given by the  $(N + N_n)$ -particle Schrödinger equation. The present paper is concerned with such an attempt. Another density functional approach to superconductivity which is, however, not entirely based on first principles, has recently been put forward by Oliveira, Gross and Kohn (1988) and Gross and Kurth (1991).

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In §2 we outline the main features of a generalized density functional theory (GDFT) the details of which have been given in previous papers by the present author (Fritsche 1986, 1991). Consequences that occur on leaving the Born–Oppenheimer (BO) approximation are discussed in §3. The principles that give rise to a gap in the electronic one-particle spectrum are described in §4. In §5 we discuss the prospects of working out further consequences of the theory.

## §2. ELEMENTS OF GENERALIZED DENSITY FUNCTIONAL THEORY

In this section we briefly discuss some relevant features of GDFT and refer the reader for details to previous papers of the present author (Fritsche 1986, 1991). A more complete report will be published elsewhere (Fritsche 1993).

We first consider a situation where the  $N_n$  atomic nuclei of the solid under study are at rest in a regular (periodic) array of positions  $\mathbf{R}_\alpha^0$ . We use the familiar notation  $\mathbf{x} = (\mathbf{r}, s)$  for real-space and spin coordinate of an electron. Stationary states

$$\Psi_n = \Psi_n(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$$

are solutions to the pertinent Schrödinger equation. If one subjects the system to an infinitesimally small perturbation, the change in  $\Psi_n$  may be written

$$\Psi'_n = \Psi_n + \eta_n \delta\Psi_n$$

where  $\eta_n$  is a positive, infinitesimally small parameter, and  $\delta\Psi_n$  is normalized to unity. The change in  $\Psi_n$  gives rise to a change in the spin-resolved one-particle density, that is

$$\delta\rho_{ns}(\mathbf{r}) = \rho'_{ns}(\mathbf{r}) - \rho_{ns}(\mathbf{r}),$$

where the primed density derives from  $\Psi'_n$ . The change in  $\rho_{2n}^{(s',s)}(\mathbf{r}', \mathbf{r})$  is defined analogously. It can be shown that the following relation holds:

$$\delta\rho_{2n}^{(s',s)}(\mathbf{r}'', \mathbf{r}') = \int \Gamma_n^{(s',s)}(\mathbf{r}'', \mathbf{r}', \mathbf{r}) \delta\rho_{ns}(\mathbf{r}) d^3r + \int \Lambda_n^{(s',s)}(\mathbf{r}'', \mathbf{r}) \delta\sigma_{ns}(\mathbf{r}) d^3r,$$

where  $\Gamma_n^{(s',s)}$  and  $\Lambda_n^{(s',s)}$  are real-valued functions and  $\delta\sigma_{ns}(\mathbf{r})$  is defined by

$$i\delta\sigma_{ns}(\mathbf{r}) = \eta_n N \int (\Psi_n^* \delta\Psi_n - \Psi_n \delta\Psi_n^*) d^4x_2 \dots d^4x_N.$$

The complex-valued function

$$G_n^{(s',s)}(\mathbf{r}'', \mathbf{r}', \mathbf{r}) = \Gamma_n^{(s',s)}(\mathbf{r}'', \mathbf{r}', \mathbf{r}) - i\Lambda_n^{(s',s)}(\mathbf{r}'', \mathbf{r}', \mathbf{r})$$

can be uniquely constructed for any eigenstate  $\Psi_n$ . If one writes the exchange–correlation energy  $E_{xc}^{(n)}$  by using the correlated two-particle density (Fritsche 1991), the variation in  $E_{xc}^{(n)}$  may be written

$$\delta E_{xc}^{(n)} = \delta E_{xc1}^{(n)} + \delta E_{xc2}^{(n)},$$

where

$$\delta E_{xc1}^{(n)} = \sum_s \int V_{xc}^{(n)}(\mathbf{r}, s) \delta\rho_{ns}(\mathbf{r}) d^3r \quad (1)$$

and

$$V_{xc}^{(n)}(\mathbf{r}, s) = \frac{1}{2} \sum_{s'} \int \frac{\Gamma_n^{(s',s)}(\mathbf{r}'', \mathbf{r}', \mathbf{r})}{|\mathbf{r}'' - \mathbf{r}'|} d^3r'' d^3r'. \quad (2)$$

The definition of  $\delta E_{xc2}^{(n)}$  is completely analogous. For the ground state ( $n=0$ ), eqn. (1) turns out to be identical with the respective equation defining the exchange–correlation potential in conventional density functional theory (DFT).

The crucial point of GDFT consists of the following observation. If one turns off the electron–electron interaction of the system under consideration and simultaneously turns on an extra potential  $\hat{V}_{\text{ext}}^{(n)}(\mathbf{r}, s)$  that conserves  $\rho_{ns}(\mathbf{r})$ , the resulting non-interacting  $N$ -electron system may be described in terms of one-particle Kohn–Sham (KS) type of equations with an effective potential  $V_{\text{eff}}^{(n)}(\mathbf{r}, s)$  given by

$$V_{\text{eff}}^{(n)}(\mathbf{r}, s) = V_{\text{ext}}^0(\mathbf{r}) + V_{\text{H}}^{(n)}(\mathbf{r}) + V_{\text{xc}}^{(n)}(\mathbf{r}, s), \quad (3)$$

where

$$V_{\text{H}}^{(n)}(\mathbf{r}) = \int \frac{\rho_n(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} d^3r'$$

is the Hartree potential associated with  $\rho_n(\mathbf{r})$ , which is just the sum of the spin-resolved densities. The potential set up by the nuclei is denoted by  $V_{\text{ext}}^0(\mathbf{r})$ . The solutions  $\psi_{\hat{n}s}(\mathbf{k}, \mathbf{r})$  to these KS equations form a complete orthonormal set which may be used to construct a complete orthonormal set of Slater determinants  $\Phi_n$  in terms of which one can expand  $\Psi_n$  in a configuration interaction (CI) series. This CI expansion has the unique property that the leading configuration, which we denote by  $\Phi_n$ , yields exactly the same one-particle density  $\rho_{ns}(\mathbf{r})$  as  $\Psi_n$  itself, that is

$$\rho_{ns}(\mathbf{r}) = N \int |\Phi_n(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)|^2 d^4x_2 \dots d^4x_N. \quad (4)$$

One may therefore rewrite the CI expansion in the form

$$\Psi_n = \Phi_n + \tilde{\Psi}_n, \quad (5)$$

where

$$\tilde{\Psi}_n = \sum_k c'_{nk} \Phi_k$$

and

$$c'_{nk} = \begin{cases} c_{nk} - 1, & \text{for } k = n, \\ c_{nk} & \text{otherwise} \end{cases}$$

Because of the latter,  $\Phi_n$  and  $\tilde{\Psi}_n$  are non-orthogonal. Equation (5) states that any  $N$ -electron eigenstate can be partitioned into a single Slater determinant and a remainder that does not contribute to the one-particle density, which means that the cross-terms between  $\Phi_n$  and  $\tilde{\Psi}_n$  plus  $|\tilde{\Psi}_n|^2$  integrate to a zero-density contribution. (In case that  $V_{\text{ext}}^0(\mathbf{r})$  has central or axial symmetry,  $\Phi_n$  may consist of a symmetry-adapted linear combination of a few determinants which differ in their highest-lying degenerate orbitals (Cordes and Fritsche (1989).) For the ground state our results are, of course, in agreement with conventional DFT.

On performing the integration on the right-hand side of eqn. (4), one arrives at

$$\rho_{ns}(\mathbf{r}) = \sum_{\substack{\hat{n}, \mathbf{k} \\ (\text{occup})}} |\psi_{\hat{n}s}(\mathbf{k}, \mathbf{r})|^2$$

which is familiar from conventional DFT for the ground state.

Summarizing the above results we can write the total energy of the system in the form

$$E_n = \langle T \rangle_n + \int \rho_n(\mathbf{r}) V_{\text{ext}}^0(\mathbf{r}) d^3r + V_c^{(n)} + E_{xc}^{(n)} + \langle \tilde{T}_{e-e} \rangle_n \quad (6)$$

where

$$\langle T \rangle_n = \sum_s \sum_i^{(N_s)} \int \psi_{is}^*(\mathbf{r}) \left(-\frac{1}{2}\nabla^2\right) \psi_{is}(\mathbf{r}) d^3r \quad (7)$$

and

$$\langle \tilde{T}_{e-e} \rangle_n = \langle T_{e-e} \rangle_n - \langle T \rangle_n,$$

with  $\langle T_{e-e} \rangle_n$  denoting the true kinetic energy of the system. As to eqn. (7) we have temporarily condensed the quantum numbers  $\hat{n}, \mathbf{k}$  into a single index  $i$ . It is possible to remove the contribution  $\langle \tilde{T}_{e-e} \rangle_n$  in eqn. (6) formally by taking advantage of the above-mentioned 'adiabatic switching' (Harris and Jones 1974). If the electron-electron interaction term in the original  $N$ -electron Hamiltonian is gradually reduced by a positive factor  $\lambda$  with the property  $0 \leq \lambda \leq 1$ , one has to turn on an additional external potential  $\langle \tilde{V}_{\text{ext}}(\lambda, \mathbf{r}, s) \rangle_n$  with increasing magnitude to ensure that  $\rho_{ns}(\mathbf{r})$  remains unchanged. The existence of such a potential for the entire range of  $\lambda$  constitutes a fundamental element of DFT but is conventionally assumed without proof. Only recently has the present author shown (Fritsche 1993) that this potential actually exists and has the form

$$\tilde{V}_{\text{ext}}^{(n)}(\lambda, \mathbf{r}, s) = (1 - \lambda)V_H^{(n)}(\mathbf{r}) + V_{xc}^{(n)}(\mathbf{r}, s) - \lambda V_{xc}^{(n)}(\lambda, \mathbf{r}, s), \quad (8)$$

where  $V_{xc}^{(n)}(\lambda, \mathbf{r}, s)$  is defined by analogy to eqn. (2). The form (8) of the extra potential ensures that  $V_{\text{eff}}^{(n)}(\mathbf{r}, s)$  does not depend on  $\lambda$  so that the states  $\psi_{\hat{n},s}(\mathbf{k}, \mathbf{r})$  and hence  $\Phi_n$  in eqn. (5) remain unchanged as  $\lambda$  is switched to zero. Since  $\Phi_n$  gives the exact one-particle density, it must become identical with the exact wavefunction for  $\lambda=0$  which refers to the interaction-free electron system under study. Hence, only the portion  $\tilde{\Psi}_n(\lambda)$  in eqn. (5) is affected by the switching and gradually vanishes as  $\lambda$  tends to zero. Invoking the Hellmann-Feynman theorem, one can show that  $E_n$  may eventually be given the form

$$E_n = \sum_s \sum_{\substack{(N_s) \\ \hat{n}, \mathbf{k} \\ (\text{occup})}} \varepsilon_{\hat{n}s}(\mathbf{k}) - \frac{1}{2} \int \rho_n(\mathbf{r}) V_H^{(n)} d^3r + \sum_s \int \rho_{ns}(\mathbf{r}) [\bar{\varepsilon}_{xc}^{(n)}(\mathbf{r}, s) - V_{xc}^{(n)}(\mathbf{r}, s)] d^3r,$$

where the exchange-correlation energy  $\bar{\varepsilon}_{xc}^{(n)}$  per particle is defined as usual except that the correlation factor  $f_{s',s}^{(n)}(\mathbf{r}', \mathbf{r})$  has to be replaced by

$$\bar{f}_{s',s}^{(n)}(\mathbf{r}', \mathbf{r}) = \int_0^1 f_{s',s}^{(n)}(\lambda, \mathbf{r}', \mathbf{r}) d\lambda.$$

For details we refer the reader again to previous articles (Fritsche 1986, 1991).

As a result of the adiabatic switching there is a one-to-one correspondence between the true eigenstates  $\Psi_n$  and  $\Phi_n$ . Hence, any  $N$ -electron eigenstate can uniquely be characterized by an  $N \times N$  Slater determinant. A particle-hole-type excitation in an extended solid may thus be mapped onto a transition  $\Phi_i \rightarrow \Phi_f$  where  $\Phi_i$  contains the  $N$  occupied Bloch orbitals characterizing the ground state, and  $\Phi_f$  differs from  $\Phi_i$  only in that one Bloch state does not occur any longer and is replaced by another (formerly

unoccupied) state. The associated change in the total energy can be calculated by forming the difference  $\Delta E = E_f - E_i$ , which represents the excitation energy for the interband transition. As has been shown by the present author (Fritsche 1991), the result can be given the form

$$\Delta E = (\epsilon_f - \epsilon_i) + \Delta_{fi}, \quad (9)$$

where

$$\Delta_{fi} = \int (|\psi_f(\mathbf{r})|^2 - |\psi_i(\mathbf{r})|^2) (2\bar{E}_{xc}^{(0)}(\mathbf{r}, s) - V_{xc}^{(0)}(\mathbf{r}, s)) d^3r,$$

with the superscript 0 referring to the ground state. If the transition takes place across the fundamental gap in semiconductors or insulators, the states  $\psi_f(\mathbf{r})$  and  $\psi_i(\mathbf{r})$  are sizeably different (in general s type against p type). In that case,  $\Delta_{fi}$  is positive and typically of the order of the gap energy  $\epsilon_g = \epsilon_f - \epsilon_i$  which explains the large 'gap discrepancies' in these materials (Fritsche 1991).

In the case of a metal,  $\Phi_i$  contains the  $N$  lowest-lying Bloch states up to an energy  $\epsilon_F$ , the Fermi energy, above which there is no finite energy gap separating occupied from unoccupied states. The lowest-lying excited states  $\Psi_f$  are characterized by determinants  $\Phi_f$  that contain Bloch orbitals with energies slightly above  $\epsilon_F$  in place of orbitals with energies slightly below  $\epsilon_F$  that occur in  $\Phi_i$ . Because of the vanishingly small energy difference  $\epsilon_f - \epsilon_i$ , the spatial variations in the orbitals differ accordingly little. Consequently,  $\Delta_{fi}$  and hence the excitation energy are vanishingly small as well. The states  $\Psi_f$  that are associated with a finite current map onto determinants  $\Phi_f$  containing Bloch states whose momentum vectors form a non-centrosymmetrical distribution in  $\mathbf{k}$  space. Since the packing of Bloch states in  $\mathbf{k}$  space is quasicontinuous, there is an associated quasicontinuous set of degenerate states  $\Psi'_f$  for a metal. Any additional weak interaction introduced in  $\mathcal{H}_c^0$  (connected, for example, with impurities) will cause the initial state  $\Psi_f$  (carrying current) to decay into a mixture of those degenerate states  $\Psi'_f$  so that the distribution in  $\mathbf{k}$  space becomes again centrosymmetrical which is associated with zero current and a maximum of the entropy of the system. This is obviously the only possible behaviour of a metal close to the ground state, that is there can be no superconductivity within the present theory based on a frozen nuclear motion. As to semiconductors and insulators, it is trivially clear that one cannot establish any departure from the centrosymmetrical  $\mathbf{k}$  space occupation in the ground state without going across the gap which only occurs above the field strength of electrical breakthrough.

Collective excitations such as plasmons, magnons or excitons are distinct from excited eigenstates  $\Psi_n$  by the property that their associated one-particle densities  $\rho_{ns}(\mathbf{r})$  are no longer invariant under the lattice translations. Hence, they correspond to states

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) = \sum_n a_n \Psi_n(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \exp\left(-\frac{i}{\hbar} E_n t\right),$$

which solve the respective time-dependent Schrödinger equation. Even when they occur as virtual excitations the wavefunction has this general form, the associated total energy for which can be cast as

$$E = E_0 + \sum_{n>0} (E_n - E_0) |a_n|^2.$$

Thus one has  $E > E_0$ , which means that the occurrence of any of these excitations leads inevitably to an increase in  $E$  above the ground state, contrary to what is needed in

establishing a new superconductivity ground state. The above consideration also applies to any other kind of electronic mechanism discussed within that context.

### §3. NON-ADIABATIC NUCLEAR MOTION

We now relax the assumption of immobile atomic nuclei fixed at their rest positions  $\mathbf{R}_x^0$ . Inclusion of the nuclear motion amounts to solving the  $(N + N_n)$ -particle Schrödinger equation the associated Hamiltonian of which is given by

$$\mathcal{H}_{\text{tot}} = \tilde{\mathcal{H}}_n^0 + \mathcal{H}_e + U_{n-n}^0,$$

with  $\mathcal{H}_e$  denoting the  $N$ -electron Hamiltonian for the general nuclear positions  $\mathbf{R}_x$ . The quantity  $U_{n-n}^0$  represents the Coulombic repulsion energy of the nuclei at their rest positions  $\mathbf{R}_x^0$ , and  $\tilde{\mathcal{H}}_n^0$  is defined by

$$\tilde{\mathcal{H}}_n^0 = \sum_{\alpha=1}^{N_n} \frac{m_e}{M_n^{(\alpha)}} \left( -\frac{1}{2} \nabla_{\mathbf{R}_\alpha}^2 \right) + \tilde{U}_{n-n},$$

where  $\tilde{U}_{n-n}$  denotes the difference  $U_{n-n} - U_{n-n}^0$ . Here  $U_{n-n}$  refers to the internuclear Coulombic repulsion energy for the general positions  $\mathbf{R}_x$ . The factor  $m_e/M_n^{(\alpha)}$  denotes the ratio of the electron mass to nucleus mass.

We confine ourselves to finding the lowest-lying eigenstate of  $\mathcal{H}_{\text{tot}}$ . Quantities referring to that solution will be labelled by a superscript 0. The BO approximation (which all electronic structure calculations of solids draw upon) is in the present context characterized by two assumptions, namely

$$\tilde{\Psi}_0(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \hat{\phi}_0(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}) \Psi_0(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (10)$$

where  $\Psi_0$  denotes the electronic wavefunction as before, and furthermore

$$\tilde{\mathcal{H}}_n^0 \hat{\phi}_0 \Psi_0 = \Psi_0 \tilde{\mathcal{H}}_0^0 \hat{\phi}_0. \quad (11)$$

The implication of the form chosen for  $\Psi_0$  in eqn. (10) is that the  $N$ -electron wavefunction adjusts adiabatically to the instantaneous nuclear positions  $\mathbf{R}_x$ . On multiplying the Schrödinger equation associated with  $\mathcal{H}_{\text{tot}}$  by  $\Psi_0^*$ , using eqns. (10) and (11) and integrating over all electron coordinates, one arrives at a Schrödinger equation for the nuclear motion:

$$\tilde{\mathcal{H}}_n \hat{\phi}_0(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}) = \tilde{E}_{n0} \hat{\phi}_0(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}), \quad (12)$$

where

$$\tilde{\mathcal{H}}_n = \tilde{\mathcal{H}}_n^0 + \tilde{E}_0$$

and

$$\tilde{E}_0 = E_{e0}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}) - E_{e0}(\mathbf{R}_1^0, \mathbf{R}_2^0, \dots, \mathbf{R}_{N_n}^0),$$

with  $E_{e0}$  denoting the total electronic energy for the nuclear positions indicated. If one expands  $\tilde{U}_{n-n} + \tilde{E}_0$  in the harmonic approximation, that is in powers of the displacements  $\mathbf{R}_x - \mathbf{R}_x^0$  up to second order, eqn. (12) can be solved and yields

$$\tilde{E}_{n0} = \frac{1}{2} \sum_{b, \mathbf{q}} \hbar \omega_b(\mathbf{q}),$$

where  $\omega_b(\mathbf{q})$  refers to the frequency of a phonon associated with wave-vector  $\mathbf{q}$  and branch  $b$ . The quantity  $\tilde{E}_{n0}$  is hence to be interpreted as the total zero-point energy for

which reason we shall denote it by  $E_{\text{phonon}}^0$ . (Although we are using dimensionless quantities throughout this paper, we tolerate here the inconsistency of writing the phonon energies in their natural dimensions just to keep the familiar notation.) The total energy of the  $(N + N_n)$ -particle system within the BO approximation is therefore given by

$$E_{\text{tot}}^{\text{BO}} = E_{e0}(\mathbf{R}_1^0, \mathbf{R}_2^0, \dots, \mathbf{R}_{N_n}^0) + U_{n-n}^0 + E_{\text{phonon}}^0, \quad (13)$$

where  $E_{e0}$  is the total electronic energy as obtained from a standard density functional calculation. The quantity  $E_{\text{tot}}^{\text{BO}}$  can be interpreted as the lowest eigenvalue of a modified Schrödinger equation for the  $(N + N_n)$ -particle system with the associated Hamiltonian

$$\mathcal{H}_{\text{tot}}^{\text{BO}} = \mathcal{H}_e^0 + U_{n-n}^0 + \tilde{\mathcal{H}}_n.$$

To go beyond the adiabatic approximation defined by this Hamiltonian, we introduce

$$\mathcal{H}'_{\text{tot}} = \mathcal{H}_{\text{tot}}^{\text{BO}} + \tilde{U}_{e-n}, \quad (14)$$

where

$$\tilde{U}_{e-n} = - \sum_{\alpha=1}^{N_n} \sum_{\nu=1}^N \left( \frac{Z_\alpha}{|\mathbf{r}_\nu - \mathbf{R}_\alpha|} - \frac{Z_\alpha}{|\mathbf{r}_\nu - \mathbf{R}_\alpha^0|} \right) \quad (15)$$

describes the electron-phonon interaction. Obviously,  $\mathcal{H}'_{\text{tot}}$  and the true Hamiltonian  $\mathcal{H}_{\text{tot}}$  differ only in  $\tilde{E}_0$  which is solely a function of the positions  $\mathbf{R}_\alpha$  and vanishes quadratically as the nuclear displacements go to zero. Since  $\tilde{E}_0$  does not depend on the electron coordinates, we may neglect this contribution in discussing the effect of  $\tilde{U}_{e-n}$ .

We make a short digression to elucidate a particular feature of dynamically coupled quantum systems. We consider two eigenfunctions  $\Psi_0$  and  $\Psi_1$  of  $\mathcal{H}_e^0$ , where the superscript 0 indicates that the nuclei are in their rest positions  $\mathbf{R}_\alpha^0$ . The associated generalized density functional images  $\Phi_0$  and  $\Phi_1$  are assumed to differ only in two Bloch states with momenta  $\mathbf{k}$  and  $\mathbf{k}'$  respectively, where the latter state occurs in  $\Phi_1$  in place of where the former appears in  $\Phi_0$ . The time-dependent Schrödinger equation connected with  $\mathcal{H}_e^0$  is satisfied by

$$\Psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N, t) = \sum_{\nu=0}^1 c_\nu \Psi_\nu(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) \exp(-i\omega_\nu t).$$

On forming the square modulus of this equation, approximating  $\Psi_0, \Psi_1$  by  $\Phi_0$  and  $\Phi_1$  respectively, and integrating over  $\mathbf{x}_2$  to  $\mathbf{x}_N$  we obtain the density

$$\rho_{ns}(\mathbf{r}, t) = \frac{N}{V} + 2|c_0^* c_1| \overline{|u_{ns}^*(\mathbf{k}', \mathbf{r}) u_{ns}(\mathbf{k}, \mathbf{r})|} \cos(\mathbf{q} \cdot \mathbf{r} - \omega t + \varphi_{01}). \quad (16)$$

If  $E_1$  and  $E_0$  are sufficiently close, we may according to eqn. (9) identify  $\omega$  as the difference  $\varepsilon_{ns}(\mathbf{k}') - \varepsilon_{ns}(\mathbf{k})$ . The volume of the lattice is denoted by  $V$ ,  $\varphi_{01}$  refers to the phase of  $c_0^* c_1$ , and the overbar indicates that we have averaged over the lattice unit cell. (Hence  $\mathbf{r}$  is only defined with an uncertainty of the cell diameter.) We have, furthermore, used

$$\psi_{ns}(\mathbf{k}, \mathbf{r}) = u_{ns}(\mathbf{k}, \mathbf{r}) \exp(i\mathbf{k} \cdot \mathbf{r}),$$

where  $u_{ns}(\mathbf{k}, \mathbf{r})$  possesses lattice periodicity, and  $\mathbf{q}$  is defined

$$\mathbf{q} = \mathbf{k} - \mathbf{k}'. \quad (17)$$

Equation (16) obviously describes a travelling density wave. As soon as one couples the electron system to the nuclear motion, this density wave is seen by the nuclei via

electron-phonon interaction. A similar consideration holds for the phonon system if we were to linearly combine two states  $\hat{\phi}_0$  and  $\hat{\phi}_1$ , which differ by a phonon of frequency  $\omega$  and wave-vector  $\mathbf{q}$ . Thus, if this interaction is to give rise to a stationary state of the entire system, one has to synchronize the variations in the two subsystems and to make their spatial variations commensurate with respect to each other, which means that one has to select certain electronic excitations to fit onto a particular phonon. As to the above example, the two Bloch states have to be chosen such that

$$\varepsilon_{n_s}(\mathbf{k}') - \varepsilon_{n_s}(\mathbf{k}) = \hbar\omega_b(\mathbf{q}), \quad (18)$$

in order to couple to the respective phonon in a stationary fashion. In forming the eigenstate  $\hat{\Psi}$  of  $\mathcal{H}'_{\text{tot}}$ , all pairs which satisfy eqn. (17) and eqn. (18) have to be accounted for.

#### §4. OCCURRENCE OF A GAP

The objective of this section is twofold. Firstly, we shall recognize that in non-adiabatically coupling the electronic system to the nuclear motion the total energy of the  $(N + N_n)$ -particle system drops below its BO value. Secondly, as a result of this process, we shall observe the formation of a gap in the spectrum of the electronic one-particle energies.

We seek the lowest-lying solution to the  $(N + N_n)$ -particle Schrödinger equation

$$\mathcal{H}'_{\text{tot}} \hat{\Psi} = E_{\text{tot}} \hat{\Psi}, \quad (19)$$

where  $\mathcal{H}'_{\text{tot}}$  is given by eqns. (14) and (15). To this purpose we expand

$$\hat{\Psi} = \sum_{\hat{\mathbf{q}}} B_{\hat{\mathbf{q}}} \hat{\Psi}_{\hat{\mathbf{q}}}, \quad (20)$$

where

$$\hat{\Psi}_{\hat{\mathbf{q}}}(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}, \mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = \Psi_{\hat{\mathbf{q}}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) [c_0 \hat{\phi}_0(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}) + c_{\hat{\mathbf{q}}}^1 \hat{\phi}_{\hat{\mathbf{q}}}^1(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}) + c_{\hat{\mathbf{q}}}^2 \hat{\phi}_{\hat{\mathbf{q}}}^2(\mathbf{R}_1, \mathbf{R}_2, \dots, \mathbf{R}_{N_n}) + \dots] \quad (21)$$

and

$$\sum_{\hat{\mathbf{q}}} |B_{\hat{\mathbf{q}}}|^2 = 1. \quad (22)$$

If we neglect  $\hat{\phi}_{\hat{\mathbf{q}}}^v$  for  $v > 1$  we have

$$|c_0|^2 + |c_{\hat{\mathbf{q}}}|^2 = 1, \quad (23)$$

where we have dropped the superscript  $v$ . Here  $\hat{\phi}_0$  denotes the ground state of the nuclear motion associated with the sum of the zero-point phonon energies, and  $\hat{\phi}_{\hat{\mathbf{q}}}^v$  represents a state which differs from  $\hat{\phi}_0$  in the presence of  $v$  additional phonons of branch  $b$  and wave-vector  $\mathbf{q}$ . The latter two characteristics have been formally absorbed in  $\hat{\mathbf{q}}$ . Since the states  $\hat{\phi}_0, \hat{\phi}_{\hat{\mathbf{q}}}^v$  form a complete orthonormal set of functions in terms of which the  $\mathbf{R}_x$  dependence of  $\hat{\phi}$  can be expanded, eqn. (20) gives a complete representation of the sought-for solution.

To bring out the relevant physics as clearly as possible, we confine the ensuing derivation to a simplified form of eqn. (20) where the sum contains one term only and  $B_{\hat{\mathbf{q}}}$  is equated to unity. Thus,  $\hat{\Psi}$  is identified with  $\hat{\Psi}_{\hat{\mathbf{q}}}$ , and we neglect  $\hat{\phi}_{\hat{\mathbf{q}}}^v$  for  $v > 1$ . We furthermore assume  $c_0$  and  $c_{\hat{\mathbf{q}}}$  to be real-valued coefficients. If we insert  $\Psi_{\hat{\mathbf{q}}}$ , given by



eqn. (21), into eqn. (19), multiply by  $[c_0\hat{\phi}_0 + c_{\hat{q}}\hat{\phi}_{\hat{q}}]^*$  from the left and integrate over all coordinates  $\mathbf{R}_\alpha$ , we obtain

$$\left( \mathcal{H}_e^0 + c_0 c_{\hat{q}} \sum_{v=1}^N \tilde{V}_n(\hat{\mathbf{q}}, \mathbf{r}_v) \cos(\mathbf{q} \cdot \mathbf{r}_v) \right) \Psi_{\hat{q}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N) = E_e(\hat{\mathbf{q}}) \Psi_{\hat{q}}(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N), \quad (24)$$

where

$$\tilde{V}_n(\hat{\mathbf{q}}, \mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r}) = -\frac{1}{2} \sum_{\alpha=1}^{N_n} Z_\alpha \int \frac{\hat{\phi}_0^* \hat{\phi}_{\hat{q}} + \hat{\phi}_{\hat{q}}^* \hat{\phi}_0}{|\mathbf{r} - \mathbf{R}_\alpha|} d^3 \mathbf{R}_1 \dots d^3 \mathbf{R}_{N_n}$$

acts as an additional external potential  $V_n(\hat{\mathbf{q}}, \mathbf{r})$  seen by the electronic system as a result of having formed a linear combination of  $\hat{\phi}_0$  and  $\hat{\phi}_{\hat{q}}$ . Hence its occurrence is completely analogous to that of the density wave discussed in the context of eqn. (16). The quantity  $E_e(\hat{\mathbf{q}})$  is defined by

$$E_e(\hat{\mathbf{q}}) = E_{\text{tot}} - U_{n-n}^0 - E_{\text{phonon}}^0 + \hbar\omega_{\hat{q}} c_{\hat{q}}^2. \quad (25)$$

Equation (24) can be handled on the same generalized density function footing as the Schrödinger equation that pertains to the adiabatic case. In going through the same arguments as considered in the previous situation, we arrive at the same one-particle equation, the only difference being that the effective potential, given by eqn. (3), now has the form

$$V_{\text{eff}}^{(\hat{\mathbf{q}})}(\mathbf{r}, s) = V_{\text{ext}}^{(\hat{\mathbf{q}})}(\mathbf{r}) + V_{\text{H}}^{(\hat{\mathbf{q}})}(\mathbf{r}) + V_{\text{xc}}^{(\hat{\mathbf{q}})}(\mathbf{r}, s), \quad (26)$$

where

$$V_{\text{ext}}^{(\hat{\mathbf{q}})}(\mathbf{r}) = V_{\text{ext}}^0(\mathbf{r}) + c_0 c_{\hat{q}} \tilde{V}_n(\hat{\mathbf{q}}, \mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r}).$$

The one-particle equation has to be solved self-consistently for the  $N$  electrons as before which amounts to solving the 'frozen-phonon problem' (for example Yin and Cohen (1980, 1982)). In a linear approximation we may describe the self-consistency-controlled response of the Hartree and exchange-correlation potential to the presence of a spatially varying extra potential by a static dielectric function  $\epsilon(\hat{\mathbf{q}}, \mathbf{r})$  such that eqn. (26) takes the form

$$V_{\text{eff}}^{(\hat{\mathbf{q}})}(\mathbf{r}, s) = V_{\text{eff}}^{(0)}(\mathbf{r}, s) + c_0 c_{\hat{q}} \tilde{V}_n^{\text{scr}}(\hat{\mathbf{q}}, \mathbf{r}) \cos(\mathbf{q} \cdot \mathbf{r}) \quad (27)$$

where

$$\tilde{V}_n^{\text{scr}}(\hat{\mathbf{q}}, \mathbf{r}) = \epsilon^{-1}(\hat{\mathbf{q}}, \mathbf{r}) \tilde{V}_n(\hat{\mathbf{q}}, \mathbf{r})$$

is the screened phonon-induced potential and  $V_{\text{eff}}^{(0)}(\mathbf{r}, s)$  refers to the unperturbed potential in the BO ground state. Given the potential from eqn. (27), we may solve the one-particle equation along the lines of the nearly free-electron (NFE) approximation, the only difference being that one has to use Bloch states pertaining to  $V_{\text{eff}}^{(0)}(\mathbf{r}, s)$  instead of free-electron states. The presence of an additional periodic potential gives rise to a gap of width

$$2\Delta_{\hat{q}} = c_0 c_{\hat{q}} \tilde{V}_n^{\text{scr}}(\hat{\mathbf{q}}) \quad (28)$$

in the original band structure  $\epsilon_{\hat{n}s}(\mathbf{k})$ , and to a departure of the new band energies  $\epsilon'_{\hat{n}s}(\mathbf{k})$  from their original values in the vicinity of the gap. ( $\tilde{V}_n^{\text{scr}}(\hat{\mathbf{q}})$  is defined as an average taken over the unit cell.) To simplify the notation we shall in the following assume a single-band situation and complete spin symmetry of the electronic system so that we may drop the suffixes  $\hat{n}$  and  $s$ . The new NFE-type states may then be written

$$\psi'(\mathbf{k}, \mathbf{r}) = u_{\mathbf{k}} \psi(\mathbf{k}, \mathbf{r}) + v_{\mathbf{k}} \psi(\mathbf{k} - \mathbf{q}, \mathbf{r}), \quad (29)$$

where

$$|u_{\mathbf{k}}|^2 + |v_{\mathbf{k}}|^2 = 1,$$

and we have accounted for eqn. (17). Obviously,  $|\psi'(\mathbf{k}, \mathbf{r})|^2$  consists of a portion that has the translational symmetry of the unperturbed lattice, and a remainder

$$2|u_{\mathbf{k}}^* v_{\mathbf{k}}| \cos(\mathbf{q} \cdot \mathbf{r} + \varphi_{\mathbf{k}})$$

which fits into the phonon-induced potential and leads to a gain of potential energy if the phase  $\varphi_{\mathbf{k}}$  is suitably chosen.

From the point of view discussed in the digression in § 3 the function  $\psi(\mathbf{k} - \mathbf{q}, \mathbf{r})$  in eqn. (29) may be interpreted as the orbital of an excited electronic configuration  $\Phi_{\mathbf{q}}$  where it occurs in correspondence to where  $\psi(\mathbf{k}, \mathbf{r})$  appears in the ground-state configuration  $\Phi_0$ . This means that  $\psi(\mathbf{k} - \mathbf{q}, \mathbf{r})$  has to be an orbital above  $\varepsilon_F$  and its energy is additionally subject to the requirement

$$\varepsilon(\mathbf{k} - \mathbf{q}) - \hbar\omega_{\mathbf{q}} = \varepsilon(\mathbf{k}),$$

as stated in eqn. (18). The energy on the right-hand side refers to the occupied counterpart orbital in  $\Phi_0$ . Hence, in calculating the total energy change under consideration, one can confine the  $\mathbf{k}$  summation over the new energies  $\varepsilon'(\mathbf{k})$  (referring to occupied states  $\psi'(\mathbf{k}, \mathbf{r})$ ) by starting downwards from the Fermi level and cutting off at an energy  $\hbar\omega_{\mathbf{q}}$  below  $\varepsilon_F$ .

For simplicity we assume a free-electron-type dependence of  $\varepsilon$  against  $\mathbf{k}$  around  $\varepsilon_F$  and introduce the quantities  $\tilde{\mathbf{k}} = \mathbf{k} - \frac{1}{2}\mathbf{q}$ ,  $\tilde{E} = \varepsilon' - \varepsilon_F$  and  $\tilde{\varepsilon} = \mathbf{q} \cdot \tilde{\mathbf{k}}$ . The results of the standard NFE calculation can then be given the form

$$\left. \begin{array}{l} |u_{\mathbf{k}}|^2 \\ |v_{\mathbf{k}}|^2 \end{array} \right\} = \frac{1}{2} \left( 1 \pm \frac{\tilde{\varepsilon}}{|\tilde{E}|} \right)$$

and

$$\tilde{E} = -(\Delta_{\mathbf{q}}^2 + \tilde{\varepsilon}^2)^{1/2},$$

where  $\Delta_{\mathbf{q}}$  is defined by eqn. (28). Since the phonon-induced potential leads only to a deformation of the occupied orbitals ( $\psi(\mathbf{k}, \mathbf{r}) \rightarrow \psi'(\mathbf{k}, \mathbf{r})$ ) and not to a change in the occupation in  $\mathbf{k}$  space, the change  $\Delta E_{e0}$  in the total electronic energy is to a very good approximation given by the sum over the differences  $\varepsilon'(\mathbf{k}) - \varepsilon(\mathbf{k})$  (Fritsche, Noffke and Eckardt 1987). As mentioned above, only states within a depth of  $\hbar\omega_{\mathbf{q}}$  below the Fermi surface are involved in the summation. If  $\hbar\omega_{\mathbf{q}} \ll \varepsilon_F$  we may give  $\Delta E_{e0}$  the form

$$\Delta E_{e0} = -N_{\mathbf{q}}^0 \int_0^{\hbar\omega_{\mathbf{q}}} (\Delta_{\mathbf{q}}^2 + \tilde{\varepsilon}^2)^{1/2} d\tilde{\varepsilon} + N_{\mathbf{q}}^0 \lim_{\Delta_{\mathbf{q}} \rightarrow 0} \left( \int_0^{\hbar\omega_{\mathbf{q}}} (\Delta_{\mathbf{q}}^2 + \tilde{\varepsilon}^2)^{1/2} d\tilde{\varepsilon} \right), \quad (30)$$

where  $N_{\mathbf{q}}^0$  denotes a reduced density of states around  $\varepsilon_F$ . (States which do not comply with eqn. (17) and eqn. (18) and the requirement that the component  $\psi(\mathbf{k} - \mathbf{q}, \mathbf{r})$  of  $\psi'(\mathbf{k}, \mathbf{r})$  must refer to a state above  $\varepsilon_F$  are given zero weight in determining  $N_{\mathbf{q}}^0$ .) If  $\Delta_{\mathbf{q}} \ll \hbar\omega_{\mathbf{q}}$ , we obtain from eqn. (30)

$$\Delta E_{e0} = -N_{\mathbf{q}}^0 \Delta_{\mathbf{q}}^2 \ln \left( \frac{2\hbar\omega_{\mathbf{q}}}{\Delta_{\mathbf{q}}} \right), \quad (31)$$

which describes an energy lowering in the electronic system. On the other hand, we have an energy increase in the phonon system described by the last term on the right-hand side of eqn. (25). If we introduce the abbreviations  $x = c_{\mathbf{q}}$  and

$$\alpha_{\mathbf{q}} = \frac{\tilde{V}_n^{\text{scr}}(\mathbf{q})}{4\hbar\omega_{\mathbf{q}}}, \quad \gamma_{\mathbf{q}} = \alpha_{\mathbf{q}} N_{\mathbf{q}}^0 \tilde{V}_n^{\text{scr}}(\mathbf{q}),$$

the total energy can be written

$$E_{\text{tot}} = E_{\text{tot}}^{\text{BO}} + \hbar\omega_{\mathbf{q}} \{x^2 + \gamma_{\mathbf{q}} x^2 (1-x^2) \ln [\alpha_{\mathbf{q}} x (1-x^2)^{1/2}]\} \quad (32)$$

where we have used eqns. (13), (23), (25) and (31). We determine the minimum of  $E_{\text{tot}}$  by forming its derivative with respect to  $x$  and equating it to zero. On the supposition that  $x$  and  $\gamma_{\mathbf{q}}$  are small compared with unity, the result may be written

$$x = \alpha_{\mathbf{q}}^{-1} \exp\left(-\frac{1}{\gamma_{\mathbf{q}}}\right) \quad (33)$$

which on resubstitution of the original quantities takes the form

$$\Delta_{\mathbf{q}} = 2\hbar\omega_{\mathbf{q}} \exp\left(-\frac{1}{N_{\mathbf{q}}^0 V_{\mathbf{q}}}\right), \quad (34)$$

where

$$V_{\mathbf{q}} = \frac{[\tilde{V}_n^{\text{scr}}(\mathbf{q})]^2}{4\hbar\omega_{\mathbf{q}}}.$$

Equation (34) is, in principle, identical with that obtained by Bardeen *et al.* (1957) although these workers use a completely different approach. If we insert the result stated by eqn. (33) into eqn. (32) and use  $x \ll 1$ , we find that the interaction of the  $N$ -electron system with the particular phonon of frequency  $\omega_{\mathbf{q}}$  leads to an energy gain of the form

$$\Delta E_{\mathbf{q}} = -\frac{1}{2} N_{\mathbf{q}}^0 \Delta_{\mathbf{q}}^2. \quad (35)$$

The principal features of the results given by eqns. (34) and (35) persist on extending the above treatment to the case where all terms on the right-hand side of eqn. (20) are included, that is when all phonons are accounted for. Details on this extension will be published elsewhere.

#### § 5. CONCLUSIONS

We have demonstrated that a generalized-density-functional based theory of superconductivity is possible. As one expects from an approach of this kind, the key quantities (notably the energy gap) can, in principle, be determined *ab initio* at the level of frozen-phonon calculations. An extension to finite temperatures is feasible along the lines of a previous paper (Fritsche 1986). One obtains equations that are essentially identical with those familiar from BCS theory. Since the electronic system forms linear combinations of states as described by eqn. (29), the associated charge density variation locks onto the phonon-induced potentials which causes a robust stiffness of the wavefunction in superconducting systems against external magnetic fields. As a result, the system will display diamagnetic properties that give rise to the Meissner effect. Surprisingly, the theory lacks any element that would reflect the importance of 'electron pairing'. Clearly, in the ground state all electronic one-particle states that occur in the generalized density functional images of  $\Psi_{\mathbf{q}}$  are equally occupied for  $s = \pm 1$  up to gap, but this is not different from the situation of a semiconductor in its

ground state. Furthermore, it turns out that the occurrence of twice the electronic charge in the flux quantum is directly connected with the phonon-induced  $v_{\mathbf{k}}$ -dependent portion of the one-particle states  $\psi'(\mathbf{k}, \mathbf{r})$ . Hence, it cannot be regarded as proving the existence of pairs. As follows from the considerations at the end of §2, the present theory leaves no room for another mechanism of superconductivity that would not be tied to the electron-phonon interaction. Since the effective coupling constant  $V_{\mathbf{q}}$  in our eqn. (34) is connected to the electron-phonon interaction in a way that is considerably different from BCS theory or from McMillan's (1968) more detailed expression for  $T_c$ , it is easy to understand why  $\Delta_{\mathbf{q}}$  (and hence  $T_c$ ) can be sizeably higher in materials where screening is much less effective than in metals. If  $\epsilon$  in a high- $T_c$  material were a factor of two lower than, for example, that in Al metal, but the other quantities defining  $\Delta_{\mathbf{q}}$  have approximately the same magnitude,  $T_c$  would be by a factor of 100 higher than for Al, that is  $T_c \approx 100$  K. Since the conductivity of high- $T_c$  materials is essentially confined to layers, that is to dimensionally reduced sections of the bulk, the magnitude of  $\epsilon(\mathbf{q})$  in the relevant regime of  $\mathbf{q}$  may well be expected to be sizeably smaller than in the bulk. Finally, there is an aspect that relates to the isotope effect. In a homonuclear superconducting material,  $\tilde{V}_n^{\text{scr}}$  can be shown to scale as  $M^{-1/4}$  with the atomic mass of the metal. Since  $\omega_{\mathbf{q}}$  scales as  $M^{-1/2}$ , one recognizes that  $V_{\mathbf{q}}$  is independent of  $M$ , and hence one has

$$T_c \propto \Delta_{\mathbf{q}} \propto M^{-1/2},$$

which describes the isotope effect. In a compound the dependences of  $(\tilde{V}_n^{\text{scr}})^2$  and  $\omega_{\mathbf{q}}$  on the atomic masses no longer cancel. The dependence of  $\Delta_{\mathbf{q}}$  (and hence  $T_c$ ) on the atomic masses is therefore no longer determined by the pre-factor of the exponential in eqn. (34). For certain materials this may well result in a much smaller  $M$  dependence of  $T_c$ , as is observed, for example, in the tungsten bronzes and the yttrium-based (1:2:3) high- $T_c$  compounds.

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