Electronic Fluctuation and the Van Der Waals Metal [and Discussion]

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Electronic fluctuation and the van der Waals metal

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Interactions determining the structure of condensed matter can systematically be developed starting with the fundamental view of such systems as neutral canonical ensembles of nuclei and electrons and proceeding to the more common viewpoint of ions and valence electrons but retaining in both the dominant fluctuational effects normally omitted.

1. Introduction

The purpose of this paper is to show that on energy scales apposite to structure in metals, bonding energies associated with electromagnetic fluctuation can be significant. In lowest order these fluctuational effects are almost universally referred to van der Waals interactions (the neutral atom case with retardation effects neglected was first worked out by London (1930)). The terminology will be extended here to systems possessing charge which is free in the normal electromagnetic sense. The issue is therefore the degree to which fluctuations in both bound and free charge can be manifested in bonding, structure, and in ordering.

The importance of electromagnetic fluctuation in the cohesive properties of the metallic state has earlier been emphasized by Rehr *et al.* (1975) and in a detailed proposal for pair interactions by Mahanty & Taylor (1978) and by Mon *et al.* (1979). The subject has recently been reviewed by Barash & Ginzburg (1988) with a focus on overall energetics. In what follows fluctuational effects are examined as a possible source of correction on energy scales that in some cases can rival those that are associated with standard mean-field-based interactions.

2. Condensed matter as a two-component system

The emphasis is to be placed on measurable structure, and it is therefore necessary to introduce from the outset a notation which links immediately to observable structural quantities. These are the one- and two-particle densities for electrons and nuclei respectively; later it will be necessary to introduce the n-particle generalizations for the composite objects referred to normally as atoms or ions. For convenience the discussion begins with a macroscopic volume Ω of an elemental system, atomic number Z_A, with N_n (10^{23}) nuclei of mass m_n having instantaneous coordinates $\boldsymbol{r}_{n1}, \ldots, \boldsymbol{r}_{nN_n}$. In a neutral canonical ensemble, there will also be present $N_e = Z_A N_n$ electrons, of mass m_e having instantaneous coordinates $\boldsymbol{r}_{e1}, \ldots, \boldsymbol{r}_{eN_e}$. For particles of type α $(\alpha = e, n)$ the one particle density operator is

$$\hat{\rho}^{(1)}_{\alpha}(\boldsymbol{r}) = \sum_{i}^{N_\alpha} \delta(\boldsymbol{r} - \boldsymbol{r}_{\alpha i}) \tag{1}$$

whose quantum statistical average over states of the entire system is

$$\rho_{\alpha}^{(1)}(\boldsymbol{r}) = \langle \hat{\rho}_{\alpha}^{(1)}(\boldsymbol{r}) \rangle \tag{2}$$

and it has the meaning that $\rho_{\alpha}^{(1)}(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$ is the probability of finding, at a given instant, a particle of type α in $\mathrm{d}\boldsymbol{r}$ at $\boldsymbol{r}$. At the level of electrons and nuclei (Chihara 1985) there are at most two-particle interactions; accordingly the two-particle density operator is also introduced

$$\hat{\rho}_{\alpha\beta}^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \hat{\rho}_{\alpha}^{(1)}(\boldsymbol{r})\,\hat{\rho}_{\beta}^{(1)}(\boldsymbol{r}') - \delta_{\alpha\beta}\,\hat{\rho}_{\alpha}^{(1)}(\boldsymbol{r})\,\delta(\boldsymbol{r}-\boldsymbol{r}'), \tag{3}$$

whose corresponding average is

$$\rho_{\alpha\beta}^{(2)}(\boldsymbol{r},\boldsymbol{r}') = \langle \hat{\rho}_{\alpha\beta}^{(2)}(\boldsymbol{r},\boldsymbol{r}') \rangle, \tag{4}$$

which has the meaning that $\rho_{\alpha\beta}^{(2)}(\boldsymbol{r},\boldsymbol{r}')\,\mathrm{d}\boldsymbol{r}\,\mathrm{d}\boldsymbol{r}'$ is the probability of finding particles of type α and β simultaneously in $\mathrm{d}\boldsymbol{r}$ and $\mathrm{d}\boldsymbol{r}'$, which are themselves separated by $\boldsymbol{r}-\boldsymbol{r}'$. For the length scales appropriate to the condensed state of matter, the nuclei are taken as point objects.

The problem is simplified in an inessential way by viewing the system as non-relativistic. If $v_{\mathrm{c}}(r) = e^2/r$ is the basic Coulomb interaction then the hamiltonian of system of electrons and nuclei can be written down, using (4) as

$$H = \sum_{\alpha}\left\{\hat{T}_{\alpha} + \tfrac{1}{2}\sum_{\beta}\int_{\Omega}\mathrm{d}\boldsymbol{r}\int_{\Omega}\mathrm{d}\boldsymbol{r}'\,v_{\mathrm{c}}(\boldsymbol{r}-\boldsymbol{r}')\,Z_{\alpha}Z_{\beta}\,\hat{\rho}_{\alpha\beta}^{(2)}(\boldsymbol{r}-\boldsymbol{r}')\right\}, \tag{5}$$

where $Z_{\mathrm{e}} = -1$ and $Z_{\mathrm{n}} = Z_{\mathrm{A}}$. Here $\hat{T}_{\alpha} = (-\hbar^2/2m_{\alpha})\,\Sigma_i \nabla_{\alpha i}^2$ are the kinetic energies; there is no explicit reference to spin. The notation introduced readily permits extension from elements to alloys or compounds.

3. Reduced hamiltonian

For elements with a relatively small number of electrons per nucleus it is now becoming possible to apply many-body quantum Monte-Carlo simulation techniques directly to (5) (Sugiyama *et al.* 1989). But with the possible exception of hydrogen ($Z_{\mathrm{A}} = 1$) (Ashcroft 1981), or with the exception of elements placed under conditions so extreme that all $N_{\mathrm{n}}Z_{\mathrm{A}}$ electrons are unbound, a description of condensed matter proceeding from (5) is not entirely appropriate. Rather (5) is modified to reflect what is known already from atomic physics, namely, that under ordinary conditions there is considerable condensation or agglomeration of electronic charge around the nuclei. In particular, for vapour phases of (5) the electronic density $\rho_{\mathrm{e}}^{(1)}(\boldsymbol{r}) = \langle \hat{\rho}_{\mathrm{e}}^{(1)}(\boldsymbol{r}) \rangle$ is extremely close to that of essentially isolated atoms. Such structure as $\rho_{\mathrm{e}}^{(1)}(\boldsymbol{r})$ possesses is just the 'shell-structure' of atomic physics (though $\rho_{\mathrm{e}}^{(1)}(\boldsymbol{r})$ is in fact remarkably devoid of structure) and, extreme conditions excepted, much of this shell structure is immune to passage of the element from vapour to condensed state. It is therefore useful to make a division of $\hat{\rho}_{\mathrm{e}}^{(1)}(\boldsymbol{r})$ into contributions arising from electrons that will exist in states dominating most aspects of the physics of condensed matter, and the remainder to be found in states bound at energies far larger than are characteristic of the condensed state. The exchange terms introduced by site identification can be incorporated within approximations that amount to a redefinition of the primary interaction, and especially its high q components (since exchange manifests itself mainly at short range). This point of view will be adopted below, in (11*a*).

The notion of valence, as applied to condensed matter must clearly be state dependent since site localization carries with it a presumption that orbitals exist whose range or scale is known. If external conditions are later imposed that require nuclei to approach closer than the diameter of such orbitals, then the system will be brought close to and beyond the onset of a Mott transition for this set of electrons. It is then appropriate to include them in the valence set, the next lower orbitals (and those below them) now constituting the localized charge. The general concept of electron-derived interactions is therefore necessarily a function of density even though for many applications this state dependence can plausibly be ignored.

With these restrictions in mind the one-particle electronic density operator is written

$$\hat{\rho}_{\mathrm{e}}^{(1)}(\boldsymbol{r}) = \sum_{i=1}^{ZN_{\mathrm{n}}} \delta(\boldsymbol{r}-\boldsymbol{r}_{\mathrm{e}i}) + \sum_{j} \sum_{i=1}^{Z_{\mathrm{c}}} \delta(\boldsymbol{r}-\boldsymbol{r}_{\mathrm{n}j}-\boldsymbol{r}_{\mathrm{e}i}^{j}), \tag{6}$$

where a number Z_{c} (of the Z_{A} per nucleus) electrons is to be in the localized (or ‘core’) class as described above, and the remainder $Z = Z_{\mathrm{A}} - Z_{\mathrm{c}}$ per nucleus are taken as valence electrons. If static conduction is eventually found to take place in the states of H, the processes will involve only the valence electrons. In what follows Z_{c}, Z (and obviously Z_{A}) are all taken to be conserved quantities.

By an ion is now meant the usual composite object formed by a nucleus together with Z_{c} electrons considered to reside in the localized states of H. To this ion can be assigned a site hamiltonian $\hat{h}_j$, which includes all electronic kinetic energies, all mutual Coulomb repulsions, and all Coulomb attractions with the nucleus. To explore the fluctuational aspects in detail, it is particularly expedient to introduce a *site density* operator

$$\hat{\rho}_{j}^{(1)}(\boldsymbol{r}) = Z\delta(\boldsymbol{r}-\boldsymbol{r}_{\mathrm{n}j}) + Z_{\mathrm{e}} \sum^{Z_{\mathrm{c}}} \delta(\boldsymbol{r}-\boldsymbol{r}_{\mathrm{n}j}-\boldsymbol{r}_{\mathrm{e}i}^{j}). \tag{7}$$

The meaning of $\hat{\rho}_{j}^{(1)}(\boldsymbol{r})$ is apparent from its Fourier representation

$$\hat{\rho}_{j}^{(1)}(\boldsymbol{q}) = \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{n}j}) \left\{ Z + \sum_{i=1}^{Z_{\mathrm{c}}} (1-\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{e}i}^{j})) \right\}, \tag{8}$$

which displays the number-fluctuations about the average valence Z. At long range ($q \rightarrow 0$)

$$e\hat{\rho}_{j}^{(1)}(\boldsymbol{q}) \approx \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{n}j}) \{ Ze + \mathrm{i}\hat{d}_j \cdot \boldsymbol{q} + \ldots \}, \tag{9}$$

where relative to the nucleus at j,

$$\hat{d}_j = \sum_{i=1}^{Z_{\mathrm{c}}} (-e)\, \boldsymbol{r}_{\mathrm{e}i}^{j}$$

is the instantaneous dipole operator giving the leading multipole correction to the standard monopole, Ze, normally assumed for such an ion

The valence electron operator is defined by

$$\hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{r}) = \sum_{i=1}^{N_{\mathrm{v}}} \delta(\boldsymbol{r}-\boldsymbol{r}_{\mathrm{e}i}), \tag{10}$$

where $N_{\mathrm{v}} = ZN_{\mathrm{n}}$. With these definitions the original hamiltonian (5) can be rewritten in a form appropriate to a description of the metallic state, namely

$$H - \sum_{j=1}^{N_{\mathrm{n}}} \hat{h}_j = \hat{T}_{\mathrm{n}} + \frac{1}{2\Omega} \sum_{z,j,j'} \hat{\rho}_j^{(1)}(\boldsymbol{q})\, \hat{\rho}_j^{(1)}(-\boldsymbol{q})\, \bar{v}(q) \tag{11a}$$

$$+\hat{T}_{\mathrm{e}} + \frac{1}{2\Omega} \sum_{q} (\hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q})\, \hat{\rho}_{\mathrm{v}}^{(1)}(-\boldsymbol{q}) - N_{\mathrm{v}})\, v_{\mathrm{c}}(q) \tag{11b}$$

$$-\frac{1}{\Omega} \sum_{q,j} \rho_{\mathrm{v}}^{(1)}(\boldsymbol{q})\, \hat{\rho}_j^{(1)}(-\boldsymbol{q})\, \omega(\boldsymbol{q}), \tag{11c}$$

where $v_{\mathrm{c}}(q) = 4\pi e^2/q^2$ and

$$\hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q}) = \sum_{i=1}^{N_{\mathrm{v}}} \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{e}i}).$$

Here $\bar{v}(q)$ incorporates the corrections, to $v_{\mathrm{c}}(q)$, for core–core exchange alluded to above. By an extension of those arguments, there is also core–valence exchange: further, in the eventual states of H, core and valence (localized and itinerant) states are orthogonal. Again, these effects are included at the level of the hamiltonian in (11 *c*) by the replacement of $v_{\mathrm{c}}(q)$ by $w(q)$, a pseudopotential (Heine 1970). In general w is a non-local operator; for small $q, Z\omega(q) \approx Zv_{\mathrm{c}}(q)$. The pseudopotential concept is by no means limited in its usefulness to simple sp metals, but has also been extended to transition metals by Moriarty (1990), and also applied in such systems to the determination of multi-centre potentials.

It is the manifestation of electromagnetic fluctuation associated with the reduced hamiltonian (11) that is of primary interest in what follows. For the most part, the length scales of interest are a few lattice constants and therefore retardation effects can be neglected. Observe that the reduced hamiltonian (11) can easily be extended to an alloy or compound metal by noting that the equivalent of (8) for component α will be

$$\hat{\rho}_{\alpha j}^{(1)}(\boldsymbol{q}) = \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{n}\alpha j}) \left\{ Z_\alpha + \sum_{i=1}^{Z_{\mathrm{c}\alpha}} (1 - \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{e}i}^{\alpha j})) \right\},$$

where Z_α is the nominal valence of each component. Charge transfer in compound or alloy formation is encompassed by assigning appropriate values to Z_α (negative values are permitted, for example). For either the single or multi-element case, (11 *c*) contains within it the physics of fluctuational attraction of an electron to a localized charge distribution and hence to the notion of electron affinity (or electronegativity).

If dipolar terms are taken to dominate the fluctuations (and hence in the expansion of (8)) then (11) becomes

$$H - \sum_{j=1}^{N_{\mathrm{n}}} \hat{h}_j = \hat{T}_{\mathrm{n}} + \frac{Z^2}{2} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\, \hat{\rho}_{\mathrm{nn}}^{(2)}(\boldsymbol{r}, \boldsymbol{r}')\, \bar{v}(\boldsymbol{r}-\boldsymbol{r}') + \tfrac{1}{2} \sum_{jj'}{}' \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}' (\hat{d}_j \cdot \nabla_{\boldsymbol{r}})\, (\hat{d}_j \cdot \nabla_{\boldsymbol{r}'})\, \bar{v}(\boldsymbol{r}-\boldsymbol{r}') \tag{11d}$$

$$+\hat{T}_{\mathrm{v}} + \tfrac{1}{2} \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\, \hat{\rho}_{\mathrm{vv}}^{(2)}(\boldsymbol{r}, \boldsymbol{r}')\, v_{\mathrm{c}}(\boldsymbol{r}-\boldsymbol{r}') + \int \mathrm{d}\boldsymbol{r} \int \mathrm{d}\boldsymbol{r}'\, \hat{\rho}_{\mathrm{n}}^{(1)}(\boldsymbol{r})\, \hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{r}')\, \omega(\boldsymbol{r}-\boldsymbol{r}') \tag{11e}$$

$$+\sum_{j} \int \mathrm{d}\boldsymbol{r}\, \hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{r})\, (\hat{d}_j \cdot \nabla_f)\, \omega(\boldsymbol{r}-\boldsymbol{r}'). \tag{11f}$$

It should be apparent that correlation effects from on-site physics are essential to (11). In this respect both the description to follow, and its consequences, differ notably from the standard Hubbard model where site-fluctuations are eliminated from the outset. The manifestation of polarizable ions in effective interactions have previously been explored for ionic crystals in what is known as the shell model (Roberts 1950).

4. Mean-field effective interactions

Implicit in the introduction of the site density operator $\hat{\rho}_j^{(1)}(\boldsymbol{r})$ (see (7)) is the adiabatic (Born–Oppenheimer) separation of timescales. For most purposes it is admissible to proceed on the solution of the states of (11) by solving an electron problem in which the nuclear densities $\hat{\rho}_{\mathrm{n}}^{(1)}(\boldsymbol{r})$, $\hat{\rho}_{\mathrm{nn}}^{(2)}(\boldsymbol{r},\boldsymbol{r}')$ are regarded as parameters. For the majority of electron states the adiabatic principle can be invoked (Moody *et al.* 1989). Within this assumption the notion of an effective hamiltonian controlling ionic motion can be developed by tracing out the electronic states (e) for each ionic or nuclear configuration (e(n)). The partition function for the system than has the form ($\beta = 1/k_{\mathrm{B}}\mathrm{T}$)

$$Z = Z(\Omega, T) = \mathrm{Tr}\,\mathrm{e}^{-\beta H}$$

$$= \mathrm{Tr}_{\mathrm{n}} \exp\left(-\beta H_{\mathrm{eff}}(\boldsymbol{r}_{\mathrm{n}i}, \ldots, \boldsymbol{r}_{\mathrm{n}N_{\mathrm{n}}}; \Omega, \beta)\right) \tag{12}$$

with
$$H_{\mathrm{eff}} = -k_B T \ln \mathrm{Tr}_{\mathrm{e(n)}} \exp\left(-\beta H(\{\boldsymbol{r}_{\mathrm{e}i}; \boldsymbol{r}_{\mathrm{n}j}\})\right).$$

In this form, the effective hamiltonian would include, in principle, contributions of entropic origin from the electronic subsystem. For many applications, however, the chosen thermodynamic conditions are such that the electron system is very close to its ground state, $\boldsymbol{\Psi}^0_{\mathrm{e(n)}}$ say, and if this is so the implied ground state trace leads to

$$H_{\mathrm{eff}}(\{\boldsymbol{r}_{\mathrm{n}j}\}; \Omega) = \hat{T}_{\mathrm{n}} + V(\boldsymbol{r}_{\mathrm{n}1}, \ldots, \boldsymbol{r}_{\mathrm{n}N_{\mathrm{n}}}; \Omega), \tag{13}$$

$$V(\boldsymbol{r}_{\mathrm{n}1}, \ldots, \boldsymbol{r}_{\mathrm{n}N_{\mathrm{n}}}; \Omega) = \langle \boldsymbol{\Psi}^0_{\mathrm{e(n)}} | H - \hat{T}_{\mathrm{n}} | \boldsymbol{\Psi}^0_{\mathrm{e(n)}} \rangle, \tag{14}$$

which is a many-body potential energy function. This result is not different from what is expected by application of the same argument to a few-body problem, say a molecule. The electron problem appears now in terms of the more familiar language of *bonds* which an appropriate resolution of $V(\{\boldsymbol{r}_{\mathrm{n}j}\}; \Omega)$ defines.

In confronting the interconnected issues of bonding and structure the assumption is usually made that $V(\{\boldsymbol{r}_{\mathrm{n}j}\}; \Omega)$ can be developed in a form

$$V(\{\boldsymbol{r}_{\mathrm{n}j}\}; \Omega) = f(\Omega) + \tfrac{1}{2}\sum_{i,j}{}' \phi^{(2)}_{ij}(\Omega) + \frac{1}{3!}\sum_{i,j,k}{}' \phi^{(3)}_{ijk}(\Omega) + \ldots, \tag{15}$$

where $f(\Omega)$ is a function of volume only (see below) and where the pair, ($\phi^{(2)}$), triplet ($\phi^{(3)}$)..., potentials are assumed to be transferable between configurations, as discussed earlier. This assumption is far from obvious, and in fact is probably not generally correct. So far as the electrons are concerned, there can be no reason to suppose that in the treatment of the statistical mechanics of the ion or nuclear system, configuration independence of the $\phi^{(n)}$ is guaranteed. The existence of transient bonding in metallic liquid states of the traditional semiconductors Si and Ge is already evidence of this (Ashcroft 1990; Štich *et al.* 1989). This point is of some importance to exercises where attempts are made to invert structural information in order to extract forms of $\phi^{(n)}$, especially $\phi^{(2)}$.

For many metals, and also their alloys, it is common practice to assume that the dynamical units of primary statistical concern are single ions, and that associated with those units are transferable potentials $\phi^{(n)}$. Among the simplest of such systems are the sp metals typified by the light alkalis, Mg, Al, and so on. For these it is also usually assumed that the ions are electronically rigid, that is, that the site fluctuations specifically retained in (11*a*) and (11*c*) are either ignorable or treatable in a mean-field way. The validity of this assumption will be taken up below, but for the present it is sufficient to note that the approximation being made is rendered by the statement

$$\hat{\rho}_j^{(1)}(\boldsymbol{q}) \rightarrow \langle \hat{\rho}_j^{(1)}(\boldsymbol{q})\rangle = \rho_j(q) = \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_{\mathrm{n}j}\, g(q)\, Z, \tag{16}$$

where $g(q)$ becomes a *static* form-factor for the ion in question (at high $q, g(q) \rightarrow 1$). Within the same approximation $\hat{h}_j$ is replaced by E_j, a constant, which can be removed by redefinition of the energy origin. Thus by ignoring electromagnetic fluctuation in the ions the hamiltonian now becomes

$$\bar{H} = \hat{T}_{\mathrm{n}} + \frac{1}{2\Omega}\sum_{\boldsymbol{q}} (\hat{\rho}_{\mathrm{n}}^{(1)}(\boldsymbol{q})\, \hat{\rho}_{\mathrm{n}}^{(1)}(-\boldsymbol{q}) - N_{\mathrm{n}})\, Z^2 \bar{v}(q) \tag{17a}$$

$$+\hat{T}_{\mathrm{v}} + \frac{1}{2\Omega}\sum_{\boldsymbol{q}} (\hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q})\, \hat{\rho}_{\mathrm{v}}^{(1)}(-\boldsymbol{q}) - N_{\mathrm{v}})\, v_{\mathrm{c}}(q) \tag{17b}$$

$$-\frac{1}{\Omega}\sum_{\boldsymbol{q}} \hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q})\, \hat{\rho}_{\mathrm{n}}^{(1)}(-\boldsymbol{q})\, \omega(q), \tag{17c}$$

where the definition of $\bar{v}(q)$ is now extended to include $g(q)$ as well. This form of hamiltonian is used both in simulation studies (for example, in the method of Car & Parinello (1985)) and also as the starting point for the formal development of multicentre interactions $\phi^{(\mathrm{n})}$ in the metallic state. The latter proceeds (Ashcroft & Stroud 1978) by separating the $q = 0$ terms in (17), which are always large, introducing a coupling constant in (17*c*), and introducing the *m*th order static response functions $\chi^{(m)}(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_m; \boldsymbol{\Omega})$ of the homogeneous electron gas hamiltonian (essentially (17*b*) with $q = 0$ terms removed). Then (Ashcroft & Langreth 1967; Brovman & Kagan 1970)

$$H_{\mathrm{eff}} = \hat{T}_{\mathrm{n}} + \frac{1}{2\Omega}\sum (\hat{\rho}_{\mathrm{n}}^{(1)}(\boldsymbol{q})\, \hat{\rho}_{\mathrm{n}}^{(1)}(-\boldsymbol{q}) - N_{\mathrm{n}})\, Z^2 \bar{v}(q)$$

$$+E_0(\bar{\rho}_{\mathrm{e}}^{(1)})\frac{1}{\Omega}\sum_{m\boldsymbol{q}}\sum_{\boldsymbol{q}_1,\ldots\boldsymbol{q}_m} \frac{1}{m+1}\chi^{(m)}(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_m)\, w(q)\, w(q_1) \ldots w(q_m)$$

$$\times\, \hat{\rho}_n^{(1)}(\boldsymbol{q})\, \hat{\rho}_n^{(1)}(\boldsymbol{q}_1) \ldots \hat{\rho}_n^{(1)}(\boldsymbol{q}_m)\, \delta(\boldsymbol{q} + \boldsymbol{q}_1 \mathrm{u}\, \boldsymbol{q}_m), \tag{18}$$

where $E_0(\bar{\rho}_e^{(1)})$ is the ground state energy of the interacting electron gas at the prescribed density $\bar{\rho}_{\mathrm{e}}^{(1)} = N_{\mathrm{v}}/\Omega$ together with the $q = 0$ residues. Note that the static response functions also depend on this density so that for the assumed metallic state, the form of (18) is just a slight generalization of (13), namely

$$H_{\mathrm{eff}} = \hat{T}_{\mathrm{n}} + f(\Omega) + \bar{V}(\boldsymbol{r}_{\mathrm{n}1}, \ldots, \boldsymbol{r}_{\mathrm{n}N_{\mathrm{n}}}; \boldsymbol{\Omega}), \tag{19}$$

where $\bar{V}$ is a state dependent many-centre potential defined via (18), and $f(\boldsymbol{\Omega})$ is a function solely dependent on density and not-derivable from sums over *n*-atom potentials. In the mean-field view, structural distinctions are made on the basis of the corresponding $\bar{V}$, a many-atom quantity. However, since a system of crystalline symmetry has been developed from a translationally invariant problem, the Fermi surface may not necessarily be given correctly. Correspondingly, the expansion (18) is then not necessarily analytic, as is known from direct summation of energies in two-band and related models. Non-analyticity is also a feature of the tight-binding approach (for example, in the dependence of energetics on coordination number).

The series represented by (18), from which pair and multicentre interactions can now be defined (V. Heine, this symposium), may be termed the mean-field result in view of its neglect of fluctuations. It has been discussed in a detailed review by Hafner (1987) and is also treated extensively in this meeting. It is sufficient to note that the pair term, also intrinsically state dependent, already has the form

$$\phi^{(2)}(r,\Omega) = \frac{Z^2e^2}{r}\left\{1-\frac{2k_{\mathrm{TF}}^2}{\pi}\int_0^\infty \mathrm{d}q\,\frac{\sin q}{q^3}\,\frac{\bar{f}(q)}{\epsilon(q,\Omega)}\left(\frac{w(q)}{Zv_{\mathrm{c}}(q)}\right)^2\right\}, \tag{20}$$

where the requisite linear response function has been written

$$\chi^{(1)}(q) = (-k_{\mathrm{TF}}^2/4\pi e^2)\bar{f}(q),$$

where k_{TF} is the Thomas–Fermi wave-vector, ϵ the static dielectric function of the electron gas, and $\bar{f}(q)$ contains all corrections (for exchange and local fields) beyond this. It is clear that at ionic separations typical of a metal, the first term in (20) leads to energies in the range of rydbergs. Yet calculated values of $\phi^{(2)}(r;\Omega)$ are in the millirydberg range, establishing thereby that at the level of *linear* response, only, the second term in (20) cancels the first to within parts per 10^3. For this reason alone contributions to structure and bonding from higher response both static and fluctuating are important to consider. The millirydberg scale of the pair potential represented by (20) provides a useful base for comparison of fluctuation based interactions.

5. Fluctuation-based interactions

The extent to which the mean field approximation implicit in assumption of an electronically rigid ion core constitutes a meaningful approximation is ultimately controlled by the magnitude of the corresponding ion polarizability $\alpha(\omega)$ in a specifically metallic environment. It is known that the polarizability of a free ion differs from that of an ion placed in a metallic environment, but unless conditions are chosen close to the onset of a Mott transition these changes are not large (Nieminen & Puska 1982). The values themselves can, however, be substantial ($\alpha(0) = 5.7a_0^3$ for K^+, for example) and the assumption of electronically rigid cores, even for some relatively common systems is therefore often difficult to justify, *a priori*. It should be remembered that a process of local polarization represents a physical mechanism in which by fluctuation charge is separated in space. Since relative displacement is involved, the process is not local and thus not representable by local approximations to true energy functionals. The point being made here is that for fixed $\hat{\rho}_{\mathrm{n}}^{(1)}$ or $\hat{\rho}_{\mathrm{nn}}^{(2)}$, the electronic problem defined by (11 *b*) and (11 *c*), and subsequently reduced to (17 *b*) and (17 *c*) is also the starting point for density functional methods. Density functional theory and its applications has been reviewed recently by Jones & Gunnarsson (1989) (see also Srivastava & Weaire 1987). Since information on exact functionals for inhomogeneous systems is lacking, approximations are usually developed that utilize the properties of the homogeneous counterpart, mainly, however, through local approximation. This approach can only include in an average way the polarization effects that are being addressed here. Similar considerations can clearly apply when charge is displaced by the polarization processes that accompany the excitations of electrons across the gap of a semiconductor.

For cohesion of the condensed state, in particular, the role of electromagnetic fluctuational effects in energetics, has been treated in depth by Barash & Ginzburg (1989). Here the focus is on the more specific problem of the detailed physical form of the microscopic interactions contributing not only to cohesion, but more especially to bonding. The most familiar case occurs when the system is taken to consist of entirely localized charge ($Z = 0$ in (8)) for which (11a) is then the only surviving term in the hamiltonian. Then as first shown by London (1930) the pairwise contribution that results is given at long range by

$$\phi_{V\mathrm{d}W}(r) = -\hbar \int_0^\infty \frac{\mathrm{d}\omega}{2\pi}\, \alpha_1(\mathrm{i}\omega)\, \alpha_2(\mathrm{i}\omega) \left\{ \left(\frac{\partial^2 v_\mathrm{c}(r)}{\partial r^2}\right)^2 + \frac{2}{r^2}\left(\frac{\partial v_\mathrm{c}(r)}{\partial r}\right)^2 \right\} \tag{21}$$

(see also Slater & Kirkwood 1937). Here r is the separation of the two localized systems whose frequency dependent polarizabilities are $\alpha_1(\omega)$ and $\alpha_2(\omega)$. An intuitive and simple limit of (21) results when the polarizability is dominated by a single excitation energy $\varDelta$. For identical ions the result is approximately

$$\phi_{V\mathrm{d}W}(r) = -\tfrac{3}{4}\varDelta(\alpha^{\frac{1}{3}}/r)^6, \tag{22a}$$

where α is the static limit of $\alpha(\omega)$. This form for $\phi_{V\mathrm{d}W}$ can be used to establish the energy scales for fluctuation based interactions in relation to their mean field counterparts whose densities are fixed in the main by $f(\varOmega)$ (see (17)). Evidently if $\varDelta$ is a few rydbergs, r a few a_0, and α for an ion a few a_0^3, then from (22a)

$$\phi_{V\mathrm{d}W} \sim O(10^{-3})\,\mathrm{Ryd}. \tag{22b}$$

Detailed comparison with (20) requires $V\mathrm{d}W$ specification if material dependent parameters (pseuodpotentials, densities, and so forth), but it is nevertheless apparent that the fluctuational and mean-field scales can be comparable. This has also been noted in an entirely classical context. In the example of ionic systems, Woodward *et al.* (1988) have shown that thermal fluctuations in mean-field response charge in counter ions assembled around macro-ions can lead to very significant dipole–dipole attraction.

The argument just given does not change in an essential way of the neutral atoms are now replaced by a neutral canonical ensemble of ions and free charge, once again represented by the full hamiltonian (11). Polarizabilities are generally smaller in positive ions than they are in the corresponding neutral atoms, but can be very significant, especially if the ion possesses a filled d-shell. From the expansion of the site charge (8), it is clear from the interaction (11c) that a monopole will be coupled to charge fluctuations on neighbouring ions. The ensuing attraction is effectively a two-particle limit of a more general three-particle interaction (see below). If the external monopole were chosen to be an additional electron the interaction would be considered part of the electron affinity (or electronegativity). At long range the attraction, for a monopole $+Ze$, has the well-known form

$$\phi_{\mathrm{md}}(r) \sim -(Ze^2/r)\,(\alpha^{\frac{1}{3}}/r)^3, \tag{23}$$

which has a scale similar to (22a); like (21) it must be terminated at short range by exchange repulsion. In highly symmetric structures the corresponding energies tend to cancel as can be seen from their formal origin as three-body interactions (Mon *et al.* 1979). For systems lacking such symmetry (quasi-crystalline states, or metallic glasses, for instance) the contributions from (23) can also be significant compared with the standard mean-field result (20).

In considering ions and free charge, rather than neutral atoms, terms (11*b*) and (11*c*) in the fluctuation hamiltonian lead immediately to additional modifications to the conventional lowest-order dispersion results (21) and (22). Let $\epsilon(\boldsymbol{q}, \omega)$ be the frequency dependent dielectric function of the uniform interaction electron gas. Then by including the screening of localized fluctuations (21) is replaced by

$$\phi_{V\mathrm{d}W}(r) = \int_0^\infty \frac{\mathrm{d}\omega}{2\pi} \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \int \frac{\mathrm{d}\boldsymbol{q}'}{(2\pi)^3} \alpha^2(\mathrm{i}\omega)\, v_{\mathrm{sc}}(q, \mathrm{i}\omega)\, v_{\mathrm{sc}}(q'; \mathrm{i}\omega) \exp{[\mathrm{i}(\boldsymbol{q}+\boldsymbol{q}')\cdot r]}\, (\boldsymbol{q}\cdot\boldsymbol{q}')^2 \qquad (24a)$$

(Mahanty & Taylor 1978; Mon *et al.* 1979; Maggs & Ashcroft 1987). Here $v_{\mathrm{sc}}(\boldsymbol{q}, \omega)$ is the screened Coulomb interaction

$$v_{\mathrm{sc}}(q, \omega) = v_{\mathrm{c}}(q)/\epsilon(q, \omega).$$

Once again, if core-fluctuations are dominated by a single frequency $\Delta/\hbar$, and if a simple hydrodynamic form for $\epsilon(q, \omega)$ is used, then the van der Waals interaction in a metallic environment is characterized by a scale

$$\phi_{V\mathrm{d}W}(r) = -\tfrac{3}{4}\Delta(\alpha^2(0)/r^6)\,(\Delta/(\Delta+\hbar\omega_{\mathrm{p}}))^3, \qquad (24b)$$

where ω_{p} is the plasma frequency of the three-dimensional electron gas (and hence $1/\omega_{\mathrm{p}}$ the corresponding characteristic timescale for adjustment of its microscopic fields). When $\Delta/\hbar > \omega_{\mathrm{p}}$ it is physically obvious that the electron gas can respond only weakly to fluctuations in the core; the expected limit, (22*a*), is therefore readily obtained from (24*b*). It is clear that for realistic choices of α, Δ and $\hbar\omega_{\mathrm{p}}$, the scale of (24*b*) may not be very different from (22*a*).

It is worth noting that in addition to the pairwise contributions (24) which has structural significance, there are also fluctuation contributions of a structure independent character. One example is the coupling of the zero-point motion of the multipole operators of the localized charge, to the plasma oscillations of the itinerant charge. If the linear response function of the latter is $\chi(q, \omega)$ then the contribution corresponding to dipolar coupling is

$$f_{\mathrm{ed}}(\Omega) = 4\pi \int_0^\infty \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \chi(q, \mathrm{i}\omega)\, \alpha(\mathrm{i}\omega)\, v_{\mathrm{c}}(q). \qquad (25)$$

As shown by Maggs & Ashcroft (1987) this can be a very substantial energy, typically above an electronvolt per electron for reasonable values of α. It quite clearly owes its origin to electronic correlation: in the mean-field sense of band theory it is partly included in the cohesive energy through the self-consistent construction of the one-electron potential. Finally, with respect to the form of valence electron coupling, (11*c*), some especially interesting comparisons can be made between displacive and fluctuational polarization for the case of crystalline order. These bear significantly on the question of electron ordering and are taken up briefly in the appendix.

6. Fluctuational interactions and nonlinear response

The dominant contribution to $\alpha(\omega)$ in an isolated atom is attributable to its outer valence electrons, i.e. to those that are least bound. Suppose that with others this atom then forms a condensed state that is found to be metallic. The valence electron charge, previously localized, has become itinerant; this component of the total electron density was designated earlier as $\langle \hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{r})\rangle$. In a metallic context it is conventionally referred to as screening charge, even though it is recognized that close to the nucleus its form is still reasonably atomic in character. Interstitially it departs from atomic form; nevertheless exactly the same question can be asked about the dynamic or fluctuational structure of $\rho_{\mathrm{v}}^{(1)}(\boldsymbol{r})$ that led in the earlier atomic context to van der Waals attraction.

Consider, first a single ion immersed in an otherwise uniform interacting electron gas. A static distribution $\rho_{\mathrm{v}}^{(1)}(\boldsymbol{r})$ is established around the ion by the arguments given above; it is spherically symmetric. The embedding electron gas is characterized by a response time ω_p – the equivalent of $\hbar/\Delta$ for the atomic case – and on timescales shorter than this, there will be microfields relative to a positive background with a full set of multipole components.

Suppose that a second ion is now introduced; it establishes its own screening charge, and once again these will also have a multipole decomposition on timescales short compared with ω_{p}. These observations are already sufficient to show that the arguments given for the atomic case, where the outer valence charge was considered localized but fluctuating, can be repeated for the case of screening charge. The viewpoint is actually very little changed; fluctuating multipole attraction is now identified with certain higher-order response terms. In fact, Maggs & Ashcroft (1987) have referred to this picture as one involving the fluctuation of pseudo-atoms, thereby extending into the dynamic régime the earlier static pseudo-atom concept of Ziman (1967). The viewpoint is an especially useful one in the context of metal–insulator transitions of the band-overlap type since the fluctuating dipole interaction is the embodiment of fluctuation physics that is common on both sides of the phase boundary (Ashcroft 1990; Goldstein *et al.* 1989).

The simplest application of this picture arises when a simple monopole (a rigid ion, or an electron) is found in the neighbourhood of a fluctuating pseudo atom. For this situation the corresponding contribution to a pair interaction has actually been discussed already, for it is nothing but the two-site limit of those terms in the response sequence (18) that are beyond linear. With this observation the source of attraction underlying the chemical concepts of electron affinity or electronegativity is also identified. It may be noted in passing that a qualitative association between the interaction of an electron with higher fluctuation processes and the occurrence of superconductive ordering has already been recorded by Luo & Wang (1987) (in the language of electron affinity) and by Ichikawa (1989) (in terms of electronegativity).

More interesting is the case where fluctuations on two sites are coupled; here a direct equivalence to (21) or (23) emerges except that the fluctuations originate with screening charge which in more common approximations is regarded as static. In the three dimensional examples so far considered, the corresponding contribution to pairwise interactions is

$$\phi_{\mathrm{ff}}(r)=\int_0^{\infty}\frac{\mathrm{d}\omega}{2\pi}\int\frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3}\int\frac{\mathrm{d}\boldsymbol{q}'}{(2\pi)^3}\,v_{\mathrm{sc}}(\boldsymbol{q}+\boldsymbol{q}',\mathrm{i}\omega)\,v_{\mathrm{sc}}(\boldsymbol{q}',-\mathrm{i}\omega)\,\omega_{\mathrm{s}}(\boldsymbol{q})$$
$$\times[\Lambda^{(3)}(\boldsymbol{q}+\boldsymbol{q}',\mathrm{i}\omega;\boldsymbol{q}',-\mathrm{i}\omega;\boldsymbol{q},0)]^2\,\mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}}, \quad (26)$$

where $\omega_{\mathrm{s}}(q)$ is now a statically screened pseudopotential. In (26) $\Lambda^{(3)}$ is the irreducible three-point function of the electron gas (Cenni & Saracco 1988). For small $\boldsymbol{q}$ and $\boldsymbol{q}'$ it behaves as $(1/\omega^2)\,\boldsymbol{q}\cdot\boldsymbol{q}'$ which may be compared with $(\alpha(0)/(\omega^2-\Delta^2))\,\boldsymbol{q}\cdot\boldsymbol{q}'$ as appropriate in the simplest approximation to the localized case. The analytic behaviour of $\phi_{\mathrm{ff}}(r)$ is again a power-law attraction at long range (*ca.* $-1/r^6$ in three dimensions). Dimensional analysis refines this power law to

$$\phi_{\mathrm{ff}}(r) \sim -Z^2(r_{\mathrm{s}}^{\frac{9}{2}}/r^6)\, h(r_{\mathrm{s}}) \tag{27}$$

in atomic units. Here $h(r_{\mathrm{s}})$ is any dimensionless function of density $(\frac{4}{3}\pi r_{\mathrm{s}}^3 a_0^3 = 1/\rho_{\mathrm{e}}^{(1)})$ and is typically of order 10^{-2} (Maggs & Ashcroft 1987). The possible numerical significance of higher-order dynamic processes has been noted by Rasolt & Geldart (1975) and also by Langreth & Vosko (1987) who also show that higher-order terms modify (27) still further but only to the extent of a logarithm. The magnitude of the fluctuation attraction (relative to mean field) is traceable to the fact that static screening is always constrained by the perfect screen sum rule ($\lim_{q\to 0} \epsilon^{-1}(q,0) \to 0$). This constraint does not hold at finite frequencies so that static interactions which involve intermediate higher-order processes can be stronger than their formal order might suggest. The major physical consequence is that in addition to mean-field results typified by (20), corrections arise from electromagnetic fluctuation in both localized charge (see (23)) and in response charge (see (26)). These can be expected to have structural significance according to circumstance, even though they may contribute little to overall cohesion in a metallic state.

7. Fluctuational attraction in the homogeneous and inhomogeneous electron gas

An attractive interaction, entirely equivalent to (26) also exists between electrons in the three dimensional electron gas, as shown also by Maggs and Ashcroft (1987). The underlying physical origin is also equivalent: around any electron is formed a static distribution of response or correlation charge $\langle \hat{\rho}_{\mathrm{ee}}^{(2)}(o,\boldsymbol{r})\rangle = \rho_{\mathrm{e}}^{(1)} g(r)$, where $g(r)$ is the pair correlation function. If the electron and surrounding correlation charge is then probed by another electron whose function is to serve as a test charge, the standard static screened interaction results and it is this combination that is controlled by the perfect screening sum rule. However, if the test electron is also accompanied by its own screening charge then fluctuations in both screening charges (or correlation shells) lead by the arguments in §6 to the long-range attraction

$$\phi_{\mathrm{eff}}(r) = \int_0^\infty \frac{\mathrm{d}\omega}{2\pi} \int \frac{\mathrm{d}\boldsymbol{q}}{(2\pi)^3} \int \frac{\mathrm{d}\boldsymbol{q}'}{(2\pi)^3} v_{\mathrm{sc}}(\boldsymbol{q}+\boldsymbol{q}', \mathrm{i}\omega)\, v_{\mathrm{sc}}(\boldsymbol{q}', -\mathrm{i}\omega)\, v_{\mathrm{sc}}(\boldsymbol{q}, 0) \times [\Lambda^{(3)}(\boldsymbol{q}+\boldsymbol{q}', \mathrm{i}\omega; \boldsymbol{q}', -\mathrm{i}\omega; \boldsymbol{q}, 0)]^2\, \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}} \tag{28}$$

and once again dimensional analysis in combination with the resulting r^{-6} power law give

$$\phi_{\mathrm{eff}}(r) \approx -(r_{\mathrm{s}}^{\frac{9}{2}}/r_{\mathrm{s}}^6)\, h(r_{\mathrm{s}}).$$

This term, which is significant in magnitude, goes considerably beyond what is expected on the basis of random-phase or related approximations to the local field problem in the interacting electron gas. Power law decay is clearly of a different analytic character from either the exponentially decaying (Thomas–Fermi) or Friedel oscillatory behaviour (Lindhard) which typify approximations to effective electron–electron interactions that normally ignore fluctuations. Its origin lies with physical processes that cannot be correctly included in the standard local applications of homogeneous electron gas results to inhomogeneous problems. Again, this is because polarization is fundamentally a process involving the relative displacement of charge, and as such is not local

Given this observation, and the product structure of the kernel in (28) an approximation that is useful in the inhomogeneous context can, however, be made. This is merely to associate separate three-point functions with each of two local densities characteristic of a pair of points in a non-uniform electron gas. Rapcewicz & Ashcroft (1990) have shown that when this procedure is applied to two isolated atoms then van der Waals attraction between the two centres is recovered, and it possesses essentially the correct magnitude. Incorporation of fluctuation therefore leads to a significant correction to the results obtained by Gordon & Kim (1972) in their study of attraction between closed shell atoms using functional methods but in a strictly local approximation. This corroborates the general point being made that functional approaches that omit fluctuations, represented here by only the simplest nonlinear corrections to response, can err qualitatively in their predictions of bonding.

Appendix A. Fluctuation and polarization in crystalline states

For crystalline states nuclear motion is usually described as an N_{n}-particle small oscillation problem in the harmonic or self-consistent harmonic approximation. In a Bravais lattice, the coordinate of an ion is normally written

$$\boldsymbol{r}_{\mathrm{n}j} = \boldsymbol{R}_j + \boldsymbol{u}_j,$$

where $\boldsymbol{R}_j = \langle \boldsymbol{r}_{\mathrm{n}j} \rangle$ is the equilibrium average of the coordinate, and defines one of the N_{n} sites of the crystal. For electronically rigid ions the first correction beyond the terms normally defining the band-structure becomes (see (13*c*))

$$\sum_j \sum_{\boldsymbol{q}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_j} \hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q})\,(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{u}_j)\,w(q). \tag{29}$$

However, if fluctuations in the ion are now restored, then (29) is replaced by

$$\sum_j \sum_{\boldsymbol{q}} \mathrm{e}^{\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_j} \hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q})\,\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{u}_j + \hat{d}_j/Ze) \tag{30}$$

to lowest order. This clearly displays the dual sources of polarization namely displacive (*ca.* $\boldsymbol{u}_j$) from phonon polarization waves, and local fluctuation (*ca.* $\hat{d}_j/Ze$). In a crystalline environment the latter also admit of waves of polarization, but in a different frequency range. The combination of the two in (30) shows very clearly the possibility of interference, the more so for lower valent materials ($Z = 1$). In an ionic crystal that is at the same time metallic the form of the electron coupling will differ from (30) in that the monopole parts can substantially cancel (depending on relative sizes of the positive and negative monopole charges). On the other hand, relative to the motion of a cell centre of mass there will also be dipolar character coupling arising from optic phonons in which these charges will now effectively add. Polar-optic coupling can therefore be especially large.

Typical values of $\langle u_j^2 \rangle^{\frac{1}{2}}$ and $\langle (d_j/Ze)^2 \rangle^{\frac{1}{2}}$ to be associated with (27) are

$$\text{(i)}\quad \langle u_j^2 \rangle^{\frac{1}{2}} = 0.24(r_{\mathrm{s}}^3/AZ)^{\frac{1}{4}} a_0,$$

where A is the nuclear mass number (a result which follows from the known moments of the Coulomb harmonic problem), and

$$\text{(ii)}\quad \langle (d_j/Ze)^2\rangle^{\frac{1}{2}} \sim a_0(2(\alpha_0/a_0)^3)\,(\bar{\Delta}(Ry))^{\frac{1}{2}},$$

where $\bar{\Delta}$ is an average excitation energy of the ion whose polarizability is α. It is not difficult, therefore, to envisage situations where these two sources of polarization lead to (*a*) comparable coupling, (*b*) displacive coupling dominating internal fluctuation (e.g. in the sp metals characterized by small α) and (*c*) internal fluctuation coupling dominating displacive (large Z, and in metals with complete or incomplete but polarizable d-shells). In the conventional view of electron pairing transitions (as in the superconductive state) it has been common to regard phonon-polarization waves (*ca.* $\boldsymbol{u}_j$) or the Fröhlich interaction (Fröhlich 1960) as the source of the requisite electron coupling. The possibility that charge fluctuation (*ca.* $\hat{d}_j/Ze$) might possibly dominate was first put forward by Little (1964) and subsequently applied to systems with itinerant and quasi-localized electrons by Geilikman (1965). An extensive discussion of the interplay of both sources of coupling in the context of specific materials, and especially layered compounds, has been given by Ginzburg & Kirzhnits (1982).

For crystalline symmetry, the localized fluctuations can also be coherent, as pointed out by Hopfield (1958), by Anderson (1963), by Lundqvist & Sjölander (1963), and by Lucas (1968). The nature of such collective excitations parallels that of the phonons; they are polarization waves resulting from dipolar coupled fluctuations on each crystalline site. A single-particle band-structure can still be defined for this case: it will arise by excerpting the zero-phonon-terms from the normal mode structure that results from coupled polarization-wave systems. Then the valence electron interaction term going beyond terms specifically included in band-structure will not be (32) but rather

$$\sum_j \sum_{\boldsymbol{q}} \mathrm{e}^{-W(q)} \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{R}_j)\,\hat{\rho}_{\mathrm{v}}^{(1)}(\boldsymbol{q})\,\mathrm{i}\boldsymbol{q}\cdot(\boldsymbol{u}_j+\hat{d}_j/Ze), \tag{33}$$

where $W(q)$ is a Debye–Waller factor corresponding to the zero-phonon contributions (Ashcroft 1989). Dynamics of both ion motion and internal charge then enter the coupling implicitly and it is evident that inferences made in such cases from, say, the isotope effect in superconductivity, and that are based on $\boldsymbol{u}_j$ alone can hardly be complete.

In three dimensions, the fluctuational polarization-wave structure is typified by an energy scale Δ, and by a dispersion $\hbar(\rho_{\mathrm{n}}\, e^2/m)^{\frac{1}{2}}$. In contrast to this, the ordinary plasmon in two dimensions has no energy gap at $q = 0$. Accordingly one may expect the coupled polarization wave system to disperse to $q = 0$ in a two-dimensional crystalline metal with localized fluctuating charge. Such modes have the capability of accepting arbitrarily small energies, as do acoustic phonons in three dimensions, which should be of some significance in low-temperature electronic transport. Though the collective dynamics of the two-dimensional electron gas are quite different from the three-dimensional case, the arguments leading to fluctuation based electronic attraction still carry through. It is general consequence of reduced dimensionality that the role of fluctuations increases relative to that of mean field. Thus, as Rapcewicz & Ashcroft (1990) show, the equivalent of (30) leads to attraction with long-ranged behaviour $-r_{\mathrm{s}}^3/r^{\frac{9}{2}}$ (compared with $-r_{\mathrm{s}}^{\frac{9}{2}}/r^6$ in three dimensions). The general arguments of Kohn & Luttinger (1965) then lead to the expectation of unstable behaviour, most notably of a pairing character.

References

Anderson, P. W. 1963 *Concepts in solids*, p. 132ff. New York: Benjamin.

Ashcroft, N. W. 1981 Ordered ground states of metallic hydrogen and deuterium. In *Physics of solids under high pressure* (ed. J. S. Schilling & R. N. Shelton), pp. 155–160. Amsterdam: North-Holland.

Ashcroft, N. W. 1989 Quantum solid behavior and the electronic structure of the light alkali metals. *Phys. Rev.* B **39**, 10552–10559.

Ashcroft, N. W. 1990 Electronic fluctuation, the nature of interactions and the structure of liquid metals. *Nuovo Cim.* D **12**, N 4–5; 597–618.

Ashcroft, N. W. & Langreth, D. 1967 Compressibility and binding energy of simple metals. *Phys. Rev.* **155**, 682–684.

Ashcroft, N. W. & Stroud, D. 1978 Theory of the thermodynamics of simple liquid metals. *Solid St. Phys.* **33**, 1–81.

Barash, Yu. S. & Ginzburg, V. L. 1989 Electromagnetic fluctuations and molecular forces in condensed matter. In *The dielectric function of condensed systems* (ed. L. V. Keldysh, D. A. Kirzhnits & A. A. Maradudin) pp. 389–457. Elsevier.

Brovman, E. G. & Kagan, Yu. 1970 Long wavelength phonons in metals. *Soviet Phys. JETP* **30**, 721–727.

Car, R. & Parrinello, M. 1985 Unified approach for molecular dynamics and density-functional theory. *Phys. Rev. Lett.* **55**, 2471–2474.

Cenni, R. & Saracco, P. 1988 Evaluation of a class of diagrams useful in many-body calculations. *Nucl. Phys.* A **487**, 279–300.

Chihara, J. 1985 Liquid metals and plasmas as nucleus–electron mixtures. *J. Phys.* C **18**, 3103–3118.

Fröhlich, H. 1960 The theory of the superconductive state. *Rep. Prog. Phys.* **24**, 1–23.

Geilikman, B. T. 1965 A possible mechanisms for superconductivity in alloys. *Soviet Phys. JETP* **21**, 796–798.

Ginzburg, V. L. & Kirzhnits, D. A. (eds) 1982 *High temperature superconductivity*. New York: Consultants Bureau.

Goldstein, R. E., Parola, A. & Smith, A. 1989 Fluctuating pseudoatoms in metallic fluids. *J. chem. Phys.* **91**, 1843–1854.

Gordon, R. G. & Kim, Y. S. 1972 Theory for the forces between closed-shell atoms and molecules. *J. chem. Phys.* **56**, 3122–3133.

Hafner, J. 1987 *From hamiltonians to phase diagrams*. Berlin: Springer-Verlag.

Heine, V. 1970 The pseudopotential concept. *Solid St. Phys.* **24**.

Hopfield, J. 1958 Theory of the contribution of excitons to the complex dielectric constant of crystals. *Phys. Rev.* **112**, 1555–1567.

Ichikawa, S. 1989 Superconductivity and optimum electronegativity. *J. Phys. Chem. Solids* **50**, 931–934.

Jones, R. O. & Gunnarsson, O. 1989 The density functional formalism, its application and prospects. *Rev. mod. Phys.* **61**, 689–745.

Kohn, W. & Luttinger, J. M. 1965 New mechanism for superconductivity. *Phys. Rev. Lett.* **15**, 524–526.

Langreth, D. & Vosko, S. H. 1987 Exact electron-gas response functions at high density. *Phys. Rev. Lett.* **59**, 497–500.

Little, W. 1964 Possibility of synthesising an organic superconductor, *Phys. Rev.* A **134**, A 1416–1424.

London, F. 1930 Zur theorie und systematik der Molekularkräfte. *Z. Phys.* **63**, 245–279.

Lucas, A. 1968 Collective contributions to the long range dipolar interaction in rare-gas crystals. *Physica* **35**, 353–368.

Lundqvist, S. & Sjölander, A. 1963 On polarization waves in van der Waals crystals. *Arkiv. Fysik* **26**, 17–34.

Luo, Q. & Wang, R. 1987 Electronegativity and superconductivity. *J. Phys. Chem. Solids* **48**, 425–430.

Maggs, A. C. & Ashcroft, N. W. 1987 Electronic fluctuation and cohesion in metals. *Phys. Rev. Lett.* **59**, 113–116.

Mahanty, J. & Taylor, R. 1978 Van der Waals forces in metals. *Phys. Rev.* **17**, 554–559.

Moody, J., Shapere, A. & Wilczek, F. 1989 Adiabatic effective lagrangians. In *Geometric phases in physics* (ed. A. Shapere & F. Wilczek), pp. 160–183. Singapore: World Scientific.

Mon, K. K., Ashcroft, N. W. & Chester, G. V. 1979 Core polarization, and the structure of simple metals. *Phys. Rev.* B **19**, 5103–5122.

Moriarty, J. 1990 Analytic representation of multi-ion interatomic potentials in transition metals. *Phys. Rev.* B **42**, 1609–1628.

Nieminen, R. & Puska, M. J. 1982 Core polarizabilities in metals. *Physica Scr.* **25**, 952–956.

Rapcewicz, C. & Ashcroft, N. W. 1990 Fluctuation attraction in condensed matter: a non-local functional approach. (Submitted.)

Rasolt, M. & Geldart, D. J. W. 1975 Gradient corrections in the exchange and correlation energy of an inhomogeneous electron gas. *Phys. Rev. Lett.* **35**, 1234–1237.

Rehr, J. J., Zaremba, E. & Kohn, W. 1975 Van der Waals forces in the noble metals. *Phys. Rev.* B **12**, 2062–2066.

Roberts, S. 1950 A theory of dielectric polarization in alkali-halide crystals. *Phys. Rev.* **77**, 258–263.

Slater, J. C. & Kirkwood, J. G. 1937 The van der Waals forces in gases. *Phys. Rev.* **37**, 682–697.

Srivastava, G. P. & Weaire, D. 1987 The theory of the cohesive energy of solids. *Adv. Phys.* **36**, 463–517.

Štich, I., Car, R. & Parrinello, M. 1990 Bonding and disorder in liquid silicon. *Phys. Rev. Lett.* **63**, 2240–2243.

Sugiyama, G., Serah, G. & Alder, B. J. 1989 Ground-state properties of metallic lithium. *Physica* A **156**, 144–168.

Woodward, C. E., Jönsson, B. & Åkesson, T. 1988 The ionic correlation contribution to the free energy of spherical double layers. *J. chem. Phys.* **89**, 5145–5152.

Ziman, J. M. 1967 Some non-structural aspects of the theory of metals. *Proc. phys. Soc.* **91**, 701–723.

Discussion

L. J. Sham (*University of California, San Diego, U.S.A.*). In the 1960s, Luttinger & Kohn found an interaction term between electrons in the homogeneous electron gas which cause $l > 0$ Cooper pairing and, thus, a superconducting instability. What is the relation between this interaction and the fluctuation term which Professor Ashcroft discussed?

N. W. Ashcroft. The term I was primarily discussing was the first of a ladder sequence and corresponds to the first of the multipole terms that result when fluctuations in normal static response is explicitly excepted from the totality of nonlinear response terms. Kohn & Luttinger do indeed include nonlinear interactions and one in particular is just the exchange modification of the fluctuating dipole–dipole contribution developed in my paper. On length scales important for the formation of a Cooper pair, this latter contribution is significantly attractive. However, to determine the likely angular momentum state it is necessary to know the form of the effective interaction at shorter length scales. This has not been settled in detail, though it is clear on general grounds that for $r < 2r_s$ (where the response charge around each of a pair of electrons begins to overlap) the attractive character must start to wash out.

P. W. Anderson (*Princeton, U.S.A.*). (1) Is this effect to some extent responsible for the high stability of certain heavy ions, so noticeable in oxide systems: such as Ba^{2+}, La^{2+}, Bi^{3+}? (2) With regard to long-range electron–electron forces, how can one justify using the lowest-order polarization bubble at very low density when the series is considered generally to be a series in powers of r_s? Incidentally, my paper shows that perturbation theory in general is in great difficulty in two dimensions in quite a deep sense.

N. W. Ashcroft. (1) The formation (and implied stability) of ions in a compound or intermetallic is associated with a charge transfer process. The ionization energy penalty that is paid is normally recouped from two sources, namely, electrostatic Madelung energy (in the state of eventual charge transfer), and electron affinity which impels the process in the first place. It is to electron affinity that my remarks on fluctuational aspect most naturally apply here. An electron placed outside a localized distribution of charge is attracted by an amount that depends on the nature of the localized charge. If the electron is subsequently bound a new distribution results with a new, and larger polarizability. A classic example is O^{2-}.

(2) In fact the diagrams discussed were not of the bubble class, but of the ladder class. The bubble class would lead to a normal static distribution of screening charge around an electron, and as such this would be constrained by the perfect screening sum-rule. The central physics of the effects being discussed here (as illustrated by the first term in the ladder sequence) is that internal dynamic loops are rife. These are not constrained by the rule, and because of this terms which have a formal order higher than bubble equivalents can actually lead to larger effects. While the r_s expansion (in two or three dimensions) might well be questioned for, say, thermodynamic functions, the focus here is on a specific subset of terms namely those of a predominantly inverse power multipole character that contribute to an effective interaction.

B. Coles (*Imperial College, London, U.K.*). Treatment of ion core fluctuations takes the polarizability as a well-defined quantity, but it depends on energy denominators which will be very different for Cu $3d^{10}$ ion or $3d^{10}4s$ atom and the 3d full core in copper metal. Does this make it impossible to use Professor Ashcroft's approach to calculate the full 3d shell contribution to cohesion of metallic copper?

N. W. Ashcroft. The polarization $\alpha(\omega)$ that enters is the one appropriate to the actual states of the system, here a metal where the electrons have been partitioned into valence and localized. Since both energy denominators and matrix elements of the dipole operator differ (for free ions and ions embedded in a metallic distribution of valence electrons) the values of $\alpha(\omega)$ indeed reflect such differences. The changes are discussed in some detail by Nieminen & Puska. A determination of the van der Waals contribution to ion–ion potentials therefore merely requires a prior determination of *in situ* ionic polarizabilities.

P. B. Allen (*SUNY, Stony Brook, New York, U.S.A.*). There are multi-atom fluctuation-induced interactions: the Axilrod–Teller term is the three-body analogue of the van der Waals r^{-6} interaction. What are the relevance and properties of these terms?

N. W. Ashcroft. Rapcewicz and I have argued that the successful determination of long-range van der Waals attraction between a pair of atoms, starting only with the properties of the homogeneous interacting electron gas, can be taken as supporting evidence for the necessity to go beyond static response in the construction of effective electron–electron interactions. If this view point is correct, then a simple logical extension of the argument also has to be correct namely that a three-atom interaction with the expected form should emerge when a third distribution of localized charge is introduced into the previous pair. This is exactly what Rapcewicz and I do discover: the three-atom interaction that emerges has precisely the Axilrod–Teller form, and once again the magnitude is quite well given, starting from electron gas information alone.