On the calculation of band energies in arrays of spherical atoms

D Langbein

Battelle-Institut eV, Frankfurt/Main, Germany

Abstract. When investigating the total energy of an ensemble of electrons, it is not always necessary to calculate the one-electron states explicitly. The summation over all electron states may rather be replaced by a contour integration around the poles of the logarithmic derivative of the dispersion function. We consider an arbitrary array of metallic atoms, whose one-electron potential can be represented by a muffin-tin potential. We construct the one-electron states in the array according to the concepts of the KKR method. However, rather than using the Green function technique, we consider the addition theorem for the spherical Bessel functions and introduce the phase shift conditions at the atomic shells. This variation of the method simplifies the summation of the total electron energy. On shifting the contour of the above complex integration to imaginary energies, we can considerably reduce the dispersion function. The resulting final energy expression converges rapidly, and clearly exhibits all the required relationships between atomic potential, Fermi energy and particle separation. The procedure used here is strictly analogous to that applied in the theory of van der Waals attraction. This enables a consistent treatment of one-electron contributions and many-electron correlation effects.

1. Introduction

The theory of van der Waals attraction has recently been extended to include multipole interactions of arbitrary order (Langbein 1973). The theory requires three steps. The first step is to solve the Helmholtz equation for the electromagnetic eigenvectors in the presence of the single particles. Exact solutions of the Helmholtz equation are known in spherical, cylindrical and rectangular coordinates. The phase shifts of these eigenvectors enforced by the particle under investigation are found from the Schrödinger equation and from the Maxwell equations in the case of molecules and macroscopic particles respectively.

The second step of the theory is to construct the eigenvectors of the Helmholtz equation in an array of particles from linear combinations of the eigenvectors in the presence of the single particles. The ingoing electromagnetic modes at a particular particle are the outgoing modes caused by the remaining particles. Provided that the addition theorem of all modes is known, one obtains the allowed eigenfrequencies of the Helmholtz equation by considering the phase shift conditions for all particles.

The van der Waals energy of the array under investigation is given by the quantum free energy of the allowed electromagnetic modes. This summation is greatly simplified if the state density integration technique introduced by van Kampen *et al* (1968) and a finite cavity are used (Richmond *et al* 1971, Langbein 1973). By shifting the contour of the resulting frequency integration to the imaginary axis, a rapidly converging integral

is obtained. An exact evaluation of eigenfrequencies is not necessary. The integrand is generally split into scattering and structure factors, with the latter decreasing exponentially with increasing separation of the particles under consideration.

The method described above for finding the allowed electromagnetic modes and the van der Waals energy in an array of particles is intimately related to investigations on one-electron orbitals and on the band energy by means of the Green function method. Consider an array of atoms, whose one-electron potential can be assumed spherically symmetric within some radius R and constant in the interspace (muffin-tin potential). It is then convenient to represent the electron orbitals in the interspace in terms of spherical Bessel functions and to account for scattering by the atoms by introducing the correct phase shifts. The application of this procedure to regular lattices was first reported by Korringa (1947) and by Kohn and Rostocker (1954) (KKR method).

The Green function method for constructing one-electron orbitals is formally equivalent to the above investigations on the eigenvectors of the Helmholtz equation. We consider the scattering of free waves by an array of particles in both cases. This formal agreement suggests that the third step of the theory on van der Waals attraction, the state density integration technique, can also be used successfully in the theory of one-electron orbitals. In this case we obtain the total band energy. We are then able to calculate the one-electron and the many-electron contributions to the total free energy via equivalent methods. We shall demonstrate in the following that this is in fact possible.

A first important difference between the two problems results from the fact that the energy integration in the one-electron case is along the straight line parallel to the imaginary axis which cuts the real axis at the Fermi energy E_F. The wavenumber of the corresponding orbitals is not purely imaginary, but has a real part proportional to the Fermi wavenumber. This causes oscillations of the total band energy depending on whether the Fermi wavelength is consistent with the characteristic particle separation. A second important difference between the two problems is the vector character of the electromagnetic modes. A correlated motion of two electrons causes a mutual orientation of orbitals (ie the multiplet contributions to the van der Waals energy depend on the angles enclosed by the interacting particles). In the one-electron case we consider only scalar wavefunctions (ie the multiplet contributions to the total band energy merely depend on the separation of the interacting atoms).

The following investigations are strictly analogous to the procedure used in the van der Waals case. Missing steps of the calculation are included in Langbein (1973).

2. Isolated atoms

We are interested in metallic species, in which the potential acting on the conduction electrons can be represented by a muffin-tin potential. In this case solid state theory has at hand two well established methods for calculating one-electron energies: the augmented plane wave method and the Korringa, Kohn and Rostocker method. Within each atomic sphere, Schrödinger's equation is solved exactly in terms of radial functions times spherical harmonics. In the interspace, these solutions are matched to free plane waves and to free spherical waves, respectively. We shall generally follow the KKR method, but introduce from the start the phase shifts caused by the single atoms rather than using the Green function technique. We are then able to consider regular lattices and disordered atomic arrays as well.

Let us consider a single atom at position **0**, with potential $V(r)$ within a sphere of radius R, and potential $V = 0$ in the exterior $r > R$. Using atomic units, we introduce Schrödinger's equation in the form

$$(-\tfrac{1}{2}\Delta + V(r) - E)|s\rangle = 0. \tag{1}$$

The spherical solutions of (1) in the exterior $r > R$ are

$$|s\rangle = f_m(kr)Y_m^\mu(\vartheta, \varphi), \tag{2}$$

where $f_m(kr)$ is a spherical Bessel function $j_m(kr)$, $y_m(kr)$ of the first or the second kind, and s represents the triplet of quantum numbers

$$s = (k, m, \mu). \tag{3}$$

The radial wavenumber k is related to the energy by

$$E = \tfrac{1}{2}k^2. \tag{4}$$

Within the sphere of radius R, we satisfy Schrödinger's equation by

$$|s\rangle = v_m(r)\, Y_m^\mu(\vartheta, \varphi) \tag{5}$$

yielding

$$\left[-\frac{1}{2}\left(\frac{1}{r}\frac{\partial}{\partial r}r\right)^2 + \frac{1}{2}\frac{m(m+1)}{r^2} + V(r) - E \right] v_m(r) = 0. \tag{6}$$

If $V(r)$ approaches the centre $r = 0$ not more rapidly than the Coulomb potential $1/r$, $v_m(r)$ can be represented by a Taylor series in r, which starts with the term r^m.

At the surface $r = R$ the radial part of the total wavefunction $|s\rangle$ and its radial derivative have to be continuous. This boundary condition fixes the phase of the external solution $f_m(kr)$. Putting

$$f_m(kr) = a_1 j_m(kr) + a_2 y_m(kr) \tag{7}$$

we find

$$\kappa_1(k, m)a_1 + \kappa_2(k, m)a_2 = 0 \tag{8}$$

where

$$\kappa_1(k, m) = \begin{vmatrix} v_m(R) & j_m(kR) \\ \dfrac{\mathrm{d}}{\mathrm{d}R}v_m(R) & \dfrac{\mathrm{d}}{\mathrm{d}R}j_m(kR) \end{vmatrix} \tag{9}$$

$$\kappa_2(k, m) = \begin{vmatrix} v_m(R) & y_m(kR) \\ \dfrac{\mathrm{d}}{\mathrm{d}R}v_m(R) & \dfrac{\mathrm{d}}{\mathrm{d}R}y_m(kR) \end{vmatrix}. \tag{10}$$

We note that the spherical Bessel functions cannot be normalized in finite space due to their asymptotic behavior at large arguments,

$$j_m(kr) \simeq (kr)^{-1}\sin(kr - m\pi/2), \qquad y_m(kr) \simeq (kr)^{-1}\cos(kr - m\pi/2).$$

The spectrum of allowed k and E values is continuous. In order to obtain normalizable functions and a discrete energy spectrum, we have to introduce a finite cavity of radius S,

at whose surface the wavefunction $|s\rangle$ vanishes. This yields the additional condition

$$j_m(kS)a_1 + y_m(kS)a_2 = 0 \tag{11}$$

which together with equation (8) determines a discrete k and E spectrum.

3. Pair states

Having found the possible eigenfunctions $|s\rangle$ in the presence of isolated atoms, we now ask for those in the presence of two identical atoms 1 and 2. We suggest that these eigenfunctions can be represented by a linear combination of atomic orbitals (LCAO). Using inversely oriented spherical coordinates at the two centres r_1 and r_2 as shown in figure 1, we put

$$|s\rangle = \sum_{j=1,2} \sum_{m=\mu}^{\infty} [a_1(m;j)j_m(k|r-r_j|) + a_2(m;j)y_m(k|r-r_j|)] \frac{Y_m^{\pm\mu}(\vartheta_j, \varphi_j)}{(m\pm\mu)!}. \tag{12}$$
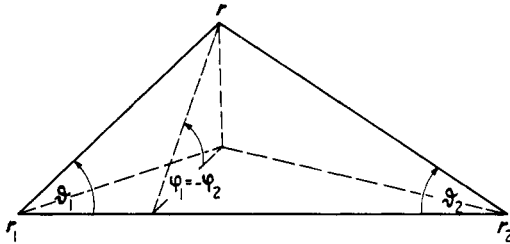
Figure 1. Inverted spherical coordinates.

The eigenfunctions (12) have to be continuous at the surface of atom 1 and of atom 2, ie they have to satisfy boundary condition (8). This is achieved by shifting the Bessel functions centred at atom 2 to atom 1, and vice versa. The addition theorem for both kinds of Bessel functions is

$$f_m(k|r-r_2|)Y_m^\mu(\vartheta_2, \varphi_2) = \sum_{n=\mu}^{\infty} (2n+1)U_{mn}^\mu(kr_{21})j_n(k|r-r_1|)Y_n^{-\mu}(\vartheta_1, \varphi_1) \tag{13}$$

where

$$U_{mn}^\mu(kr_{21}) = \left(\frac{2}{kr_{21}}\right)^\mu \sum_{v=0}^{m-\mu} (-1)^v \frac{\Gamma(m-v+\tfrac{1}{2})\Gamma(n-v+\tfrac{1}{2})\Gamma(\mu+v+\tfrac{1}{2})}{\Gamma(m+n-\mu-v+\tfrac{3}{2})\Gamma(\mu+\tfrac{1}{2})\Gamma(\tfrac{1}{2})}$$

$$\times \frac{(m+n-v)!}{(m-\mu-v)!(n-\mu-v)!v!}(m+n-\mu-2v+\tfrac{1}{2})f_{m+n-\mu-2v}(kr_{21}) \tag{14}$$

and $r_{21} = r_2 - r_1$. The expansion of orbitals centred at r_2 at the exterior position r_1 renders Bessel functions $j_n(kr)$ of the first kind only. When applying boundary condition (8) at the surface of atom 1 we conveniently include these terms in effective amplitudes $a_1(m;1)$. Satisfying boundary condition (8) at the surface of atom 2 is achieved in a similar manner by interchanging 1 and 2.

Since we are dealing with identical spherical atoms, we can use the invariance against reflection at the central plane for a classification of orbitals. They are even or odd on reflection, ie we may simplify the set of boundary conditions by using

$$a_l(m; 2) = \pm a_l(m; 1), \qquad l = 1, 2. \tag{15}$$

We finally obtain

$$\kappa_1(k, m)\left(a_1(m; 1) \pm (2m+1) \sum_{n=\mu}^{\infty} \frac{(m-\mu)!}{(n+\mu)!} \sum_l a_l(n; 1) U_{nm;l}^{\mu}(kr_{21})\right) + \kappa_2(k, m)a_2(m; 1) = 0 \tag{16}$$

where $U_{mn;l}^{\mu}(kr_{21})$, $l = 1, 2$ results from equation (14) by substituting Bessel functions $j_m(kr_{21})$ and $y_m(kr_{21})$ of the first and second kind.

Boundary conditions (16) yield M equations for the $2M$ coefficients $a_1(m; 1)$ and $a_2(m; 1)$, $M \to \infty$. In order to obtain normalized orbitals and a discrete rather than a continuous energy spectrum, we may again use the cavity and require phase relations (11). We find that each of the energy levels obtained in the presence of one atom splits up into two levels in the presence of two atoms.

In contrast to the usual LCAO method, which starts with fixed atomic orbitals and determines the optimum coefficients from the variational principle, we solve Schrödinger's equation rigorously by properly adapting the phase of the orbitals considered. This adaptability of external orbitals follows from the energy spectrum being continuous. We are free to diagonalize the orbitals with respect to the total potential.

4. Multiplet states

The construction of orbitals in the presence of an arbitrary array of atoms is equivalent to that in the presence of two atoms. We use an LCAO method in which the phase of the atomic orbitals is adaptable to the total potential. Let the centre of atom j be r_j. Since the connecting line $r_i - r_j$ between atoms i and j is no longer a symmetry axis of the array, we have to extend the summation of atomic orbitals over the rotation wavenumber μ as well and obtain

$$|s\rangle = \sum_j \sum_{m,\mu} [a_1(m, \mu; j)j_m(k|r - r_j|) + a_2(m, \mu; j)y_m(k|r - r_j|)] \frac{Y_m^{\mu}(\vartheta_j, \varphi_j)}{(m+\mu)!}. \tag{17}$$

Satisfying boundary conditions (8) at the surface of any particular atom i requires translation of the orbitals centred at atoms j to atom i. This is generally possible by means of addition theorem (13). However, in an arbitrary array of atoms we cannot introduce inversely oriented spherical coordinates for every pair of atoms. We have to start with spherical coordinates in a standard direction n, rotate those at atom j in the direction of the connecting line $r_i - r_j$ to atom i, apply addition theorem (13), and rotate the coordinates back into the standard direction n. This rotation of spherical coordinates mixes spherical harmonics of different order and equal degree. When rotating the coordinates at r_j from the standard direction n to the connecting line $n_1 = (r_i - r_j)/|r_i - r_j|$ we find from figure 2,

$$\frac{Y_m^{\mu}(\vartheta, \varphi)}{(m+\mu)!} = \sum_{\nu=-m}^{+m} C(m, \mu, \nu, \theta) \frac{Y_m^{\nu}(\vartheta_1, \varphi_1)}{(m+\nu)!}. \tag{18}$$
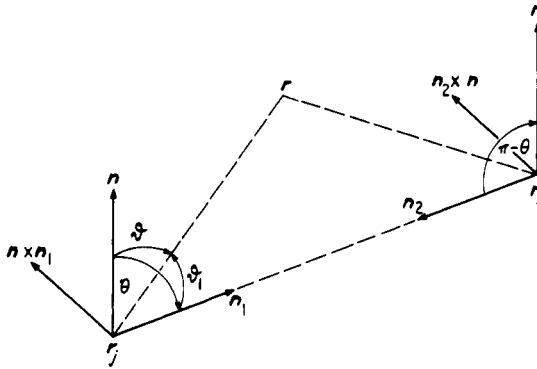
Figure 2. Rotation to $n_1 = r_i - r_j$.

ϑ, φ and ϑ_1, φ_1 are the angles of an arbitrary vector r with respect to systems n and n_1. The azimuths φ and φ_1 are measured relative to $n \times n_1$ in both systems. θ is the angle between directions n and n_1.

The coefficients $C(m, \mu, \nu, \theta)$ can be represented by Jacobi polynomials of argument $\sin^2(\tfrac{1}{2}\theta)$. We find

$$C(m, \mu, \nu, \theta) = (\cos \tfrac{1}{2}\theta)^{\mu+\nu} \frac{(m-\nu)!}{(m+\mu)!} \sum_{\lambda} \frac{(-1)^{\lambda}(2m-\lambda)!(\sin \tfrac{1}{2}\theta)^{2m-2\lambda-\mu-\nu}}{(m-\mu-\lambda)!(m-\nu-\lambda)!\lambda!} \tag{19}$$

Using rotation theorem (18) for the rotation of coordinates from n to n_1, addition theorem (13) for the translation from r_j to r_i, and again rotation theorem (18) for the inverse rotation from $n_2 = -n_1$ to n, we obtain

$$f_n(k|r-r_j|) \frac{Y_n^{\nu}(\vartheta_j, \varphi_j)}{(n+\nu)!} = \sum_{m,\mu} U(n, \nu; m, \mu; r_{ji}) j_m(k|r-r_i|) \frac{Y_m^{\mu}(\vartheta_i, \varphi_i)}{(m+\mu)!} \tag{20}$$

where

$$U(n, \nu; m, \mu; r_{ji})$$
$$= (2m+1) \sum_{\lambda} e^{i\nu\phi} C(n, \nu, \lambda, \theta) \frac{(m-\lambda)!}{(n+\lambda)!} U_{nm}^{\lambda}(kr_{ji}) C(m, -\lambda, \mu, \pi-\theta) e^{-i\mu\phi}. \tag{21}$$

ϕ is the azimuth of $n \times n_1$ in the standard system n, and $r_{ji} = r_j - r_i$.

The transformation of all orbitals centred at atoms j to atom i yields numerous additional terms $j_m(k|r-r_i|)$. Boundary condition (8) at the surface of atom i thus takes the form

$$\kappa_1(k, m)\left(a_1(m, \mu; i) + \sum_{j \neq i} \sum_{n,\nu} \sum_{l} a_l(n, \nu; j) U_l(n, \nu; m, \mu; r_{ji})\right) + \kappa_2(k, m) a_2(m, \mu; i) = 0 \tag{22}$$

with $U_l(n, \nu; m, \mu; r_{ij})$ resulting from equation (21) by substituting Bessel functions $j_m(kr_{ji})$ and $y_m(kr_{ji})$ of the first and second kind.

In the presence of two atoms we found the rotation to be a possible symmetry operation and a coupling of orbitals with equal rotational wavenumber μ. In the

presence of a multiplet of atoms we find coupling of all orbitals m and μ. Boundary conditions (22) provide $NM(2M+1)$ equations for the $2NM(2M+1)$ coefficients $a_l(m, \mu; j)$, where N is the number of atoms, $l = 1, 2$, and $M \to \infty$. We again use the auxiliary boundary conditions caused by the cavity and find that each of the discrete levels obtained in the presence of an isolated atom splits up into a band.

If the atomic array under investigation is a regular lattice, we learn from its invariance on translation by any lattice vector that we may classify the orbitals (17) according to Bloch's theorem. Putting

$$a_l(m, \mu; j) = e^{i\mathbf{q} \cdot \mathbf{r}_j} a_l(m, \mu), \qquad l = 1, 2 \tag{23}$$

we find that boundary conditions (22) no longer depend on the choice of the particular atom i, to which we transposed the orbitals. The secular determinant given by equations (22) and (11) now separates into a product of secular determinants, each corresponding to a particular wavenumber $\mathbf{q}$. We recover the secular determinant which arises on application of the KKR method.

5. Complex integration

In the investigations described so far we did not ask whether the orbitals considered have low energy and show high electron density close to the centres $\mathbf{r}_j$, or whether they have high energy and show an increased electron density in the interspace. The reason is that we intend to calculate the total band energy rather than the individual electron orbitals. We shall not solve equation (22) explicitly for all amplitudes $a_l(m, \mu; i)$, but are mainly interested in the effect of the level splitting on the total energy.

Let us calculate the total free energy of the electrons in the atomic array under consideration relative to the case of infinite separation. By relating the free energy to this limit we are not implying that the muffin-tin potentials used can be separated to infinity. This reference point is rather suggested for the sake of mathematical simplicity. Occupation of the one-electron levels resulting from (22) according to the Fermi distribution yields

$$\Delta E = \sum_{\text{all levels}} \left[kT \ln \left[1 + \exp \left(-\frac{E - E_F}{kT} \right) \right]^{-1} \right]_{\text{inf}}^{\text{fin}}. \tag{24}$$

In investigations into the theory of van der Waals attraction it was found convenient to integrate sums like (24) by means of complex integration techniques. The basic idea is to replace the state density entering (24) by an integral around the poles of the one-electron dispersion function. We introduce the analytical identity

$$\sum_{\text{zeros}} F(E_m) - \sum_{\text{poles}} F(E_n) = (2\pi i)^{-1} \oint dE \, F(E) \frac{d \ln G(E)}{dE} \tag{25}$$

where E_m runs over all zeros and E_n runs over all poles of $G(E)$ within the contour of integration. This contour, on the other hand, must not contain poles of $F(E)$. If $G(E)$ is chosen such that its zeros and poles yield the one-electron energy levels for finite and infinite separation of the atoms, we can use (25) directly for summing (24).

This objective is achieved if

$$F(E) = kT \ln \left[1 + \exp\left(-\frac{E - E_F}{kT} \right) \right]^{-1} \tag{26}$$

and if $G(E)$ equals the ratio of the secular determinants resulting from (22) and (11) for finite and infinite separation. The contour of integration has to enclose the real energy axis, but must exclude all poles

$$E_n = E_F + 2\pi i(n + \tfrac{1}{2})kT \tag{27}$$

of the Fermi distribution. This is true for the contour shown in figure 3. Hence,

$$\Delta E = (2\pi i)^{-1} \oint dE \, kT \ln \left[1 + \exp\left(-\frac{E - E_F}{kT} \right) \right]^{-1} \frac{d \ln G(E)}{dE}. \tag{28}$$
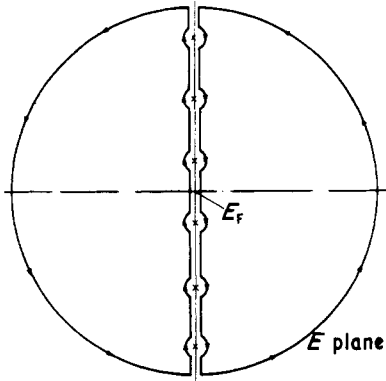
Figure 3. Contour of integration.

The integrals over the semicircles shown in figure 3 vanish with increasing radius $|E|$. We are left with the integration around the poles (27) of the Fermi distribution, and obtain by partial integration

$$\Delta E = -(4\pi i)^{-1} \oint dE \, \tanh\left(\frac{E - E_F}{2kT} \right) \ln G(E) \tag{29}$$

and

$$\Delta E = kT \sum_{n=-\infty}^{+\infty} \ln G(E_n). \tag{30}$$

We note from equation (30) that in investigations into the total band energy ΔE it is not necessary to solve the secular system (22), (11) explicitly. It is sufficient to know the ratio $G(E)$ of the secular determinants for finite and infinite separation at the poles E_n of the Fermi distribution.

If the atomic array considered is a regular lattice we find from the splitting of $G(E)$ into a product of secular determinants $G(E, q)$

$$\Delta E = (2\pi)^{-3} \int dq \, kT \sum_{n=-\infty}^{+\infty} \ln G(E_n, q) \tag{31}$$

where the integration over the wavenumber q covers one cell of the reciprocal lattice.

A representation of the integrated density of states $\ln G(E)$ by a secular determinant equivalent to equation (22) and (11) was first reported by Lloyd (1967). Similar conclusions have been drawn for arbitrary atomic arrays and regular lattices. The present procedure differs from Lloyd's treatment by explicitly using the addition theorem (13) for spherical Bessel functions and the phase shift condition (8). This makes it possible to increase the size of the cavity towards infinity and correspondingly to reduce the secular determinant.

6. Band energies

At the poles E_n of the Fermi distribution we find k to be complex owing to the complexity of the energy. Putting

$$k = k' + ik'' \tag{32}$$

we obtain from (4) and (27)

$$\begin{aligned} k' &= \{[E_F^2 + (2\pi kT)^2(n+\tfrac{1}{2})^2]^{1/2} + E_F\}^{1/2} \\ k'' &= \{[E_F^2 + (2\pi kT)^2(n+\tfrac{1}{2})^2]^{1/2} - E_F\}^{1/2}. \end{aligned} \tag{33}$$

The real part k' is equal to or larger than the Fermi wavenumber $(2E_F)^{1/2}$, the imaginary part approximately equals $[2\pi kT(n+\tfrac{1}{2})]^{1/2}$.

Complex values of k entail an important simplification of the normalization condition (11). We may now turn directly to the limit of infinite cavities and find

$$\lim_{s \to \infty} \frac{a_2(m, \mu; j)}{a_1(m, \mu; j)} = \pm i \qquad \text{for} \quad k'' \gtrless 0. \tag{34}$$

Substitution of (34) into (17) and (22) only leaves spherical Bessel functions

$$h_m^{(1,2)}(kr) = j_m(kr) \pm i y_m(kr)$$

of the third kind. These functions decrease exponentially for complex k and increasing r and thus simplify the addition theorem (13) considerably. Hence,

$$U_{mn}^{\mu}(kr) = \frac{\exp(-k''r \pm ik'r)}{(\pm i)^{m+n+2}}$$
$$\times \left[\frac{(m+\mu)!(n+\mu)!}{2^{\mu}\mu!(m-\mu)!(n-\mu)!} \frac{1}{(k''r \mp ik'r)^{\mu+1}} + O\left(\frac{1}{(k''r \mp ik'r)^{\mu+2}}\right) \right]. \tag{35}$$

$U_{mn}(kr_{ji})$ and $U(n, v; m, \mu; r_{ji})$ decrease exponentially with increasing k'' and with increasing separation r_{ji}; this ensures rapid convergence of the sum over the poles E_n

in (30). Negative values of n entail the minus sign in (34) and the use of $h_m^{(2)}(kr)$. We end up with the lower sign in (35), ie the terms $(n+\frac{1}{2})$ and $-(n+\frac{1}{2})$ render complex conjugate contributions.

Since for infinite separation all terms $U(n, v; m, \mu; r_{ji})$ vanish, the ratio of secular determinants resulting from (22) for finite and infinite separation is equal to the determinant

$$[G(E)]_{m,\mu,i;n,v,j} = \delta_{mn}\delta_{\mu v}\delta_{ij} + \frac{\kappa_1(k, m)}{\kappa_1(k, m) \pm i\kappa_2(k, m)} U(n, v; m, \mu; r_{ji}). \tag{36}$$

Equations (30) and (36) provide the total band energy of the array of particles considered. Summation over the poles E_n of the Fermi distribution is essentially an integration along that straight line parallel to the imaginary axis which cuts the real axis at the Fermi energy E_F. The main contribution to this integral results from low values of n, while increasing values of n entail an exponential decrease of the off-diagonal elements of $G(E)$. Since for low values of n we find the off-diagonal elements of $G(E)$ to oscillate like $\exp(ik'r_{ji})$, it is concluded that the total band energy ΔE also exhibits oscillations, depending on how the Fermi wavelength compares with the characteristic particle separation.

When considering a regular lattice we may replace equation (36) by

$$[G(E, q)]_{m,\mu;n,v} = \delta_{mn}\delta_{\mu v} + \frac{\kappa_1(k, m)}{\kappa_1(k, m) \pm i\kappa_2(k, m)} \sum_{j \neq i} e^{iq \cdot r_{ji}} U(n, v; m, \mu; r_{ji}). \tag{37}$$

The oscillations of the total band energy of a given lattice structure with varying Fermi energy E_F imply that changes in the Fermi energy may favour another lattice structure. Equations (31) to (37) enable us to investigate the relationships between Fermi energy, atomic pseudopotentials and lattice structure. The evaluation of the rapidly converging integral (31) relieves us from an exact calculation of the electron levels.

7. Perturbation theory

To get an idea of the results of an exact evaluation of equations (30), (31), let us consider a regular lattice and expand $\ln G(E, q)$ up to terms quadratic in the scattering amplitudes. We find from (37)

$$G(E, q) \simeq \prod_{m,\mu} \left(1 + \frac{\kappa_1(k, m)}{\kappa_1 \pm i\kappa_2} \sum_{j \neq i} e^{iq \cdot r_{ji}} U(m, \mu; m, \mu; r_{ji}) - \sum_{n,v} \frac{\kappa_1(k, m)}{\kappa_1 \pm i\kappa_2} \right.$$
$$\left. \times \sum_{j \neq i} e^{iq \cdot r_{ji}} U(n, v; m, \mu; r_{ji}) \frac{\kappa_1(k, n)}{\kappa_1 \pm i\kappa_2} \sum_{k \neq i} e^{iq \cdot r_{ki}} U(m, \mu; n, v; r_{ki}) \right) \tag{38}$$

and

$$\ln G(E, q) \simeq \sum_{m,\mu} \frac{\kappa_1(k, m)}{\kappa_1 \pm i\kappa_2} \sum_{j \neq i} e^{iq \cdot r_{ji}} U(m, \mu; m, \mu; r_{ji}) - \frac{1}{2} \sum_{m,\mu} \sum_{n,v} \frac{\kappa_1(k, m)}{\kappa_1 \pm i\kappa_2}$$
$$\times \sum_{j \neq i} e^{iq \cdot r_{ji}} U(n, v; m, \mu; r_{ji}) \frac{\kappa_1(k, n)}{\kappa_1 \pm i\kappa_2} \sum_{k \neq i} e^{iq \cdot r_{ki}} U(m, \mu; n, v; r_{ki}). \tag{39}$$

The linear terms in (39) vanish on summation over q over one reciprocal lattice cell. Of the quadratic terms, only those are left which satisfy $r_{ji} + r_{ki} = 0$. Hence,

$$\Delta E = \frac{1}{8\pi i} \oint dE \tanh\left(\frac{E - E_F}{2kT}\right) \sum_{j \neq i} \sum_{m,\mu} \sum_{n,\nu} \frac{\kappa_1(k, m)}{\kappa_1 \pm i\kappa_2} U(n, \nu; m, \mu; r_{ji})$$

$$\times \frac{\kappa_1(k, n)}{\kappa_1 \pm i\kappa_2} U(m, \mu; n, \nu; r_{ij}). \tag{40}$$

As a result of expanding $\ln G(E, q)$ up to quadratic terms, we are left with the pair contributions to the total interaction energy. Keeping the cubic terms implies inclusion of triplet contributions, and so on.

The restriction to pair contributions enables a further simplification of equation (40). In this limit it is not necessary to introduce the standard coordinate system n at all atoms j. Instead, spherical coordinates directed towards the distinct atom i can be used. One recovers boundary conditions (16) for each pair orbital and the total band energy from a summation over all pairs.

The corresponding elimination of the standard coordinate system n from energy expression (40) is achieved by summation over the rotational wavenumbers μ and ν. Substituting (21) into (40), we find the azimuths of $n \times (r_j - r_i)$ and $n \times (r_i - r_j)$ to cancel except for π. Then, using

$$\sum_{\mu} (-1)^{m-\mu} C^*(m, \nu, \mu, \theta) C(m, \mu, -\lambda, \pi - \theta) = \delta_{\nu\lambda} \tag{41}$$

we obtain

$$\Delta E = \frac{1}{8\pi i} \oint dE \tanh\left(\frac{E - E_F}{2kT}\right) \sum_{j \neq i} \sum_{m,n} \frac{\kappa_1(k, m)}{\kappa_1 \pm i\kappa_2} \frac{\kappa_1(k, n)}{\kappa_1 \pm i\kappa_2} \sum_{\lambda} (2m + 1) U_{nm}^{\lambda}(kr_{ji})$$

$$\times (2n + 1) U_{mn}^{-\lambda}(kr_{ji}). \tag{42}$$

The final expression (42) for the total band energy ΔE in a regular lattice is clearly split into phase shift and structure factors. The phase shift factor $\kappa_1(k, m)/(\kappa_1(k, m) \pm i\kappa_2(k, m))$ describes the form and strength of the potential. Its value distinguishes sharply between localized and non-localized orbitals. The structure factor $U_{nm}^{\lambda}(k, r_{ji})$ tests the lattice structure. It checks whether those orbitals which experience large phase shifts at the individual atoms cancel or add up by multiple scattering. The critical wavelength is the Fermi wavelength $2\pi/(2E_F)^{1/2}$.

8. Conclusions

The present investigations into one-electron orbitals for arrays of atoms which exhibit muffin-tin potentials are basically equivalent to the KKR method. However, rather than applying the Green function technique, we prefer to use the addition theorem for the spherical Bessel function considered and to satisfy the phase shift conditions at the atomic shells. This variation of the method pays off when the total electron energy is calculated. We replace the summation over all electron states by a contour integration over the logarithmic derivative of the electron dispersion function. By shifting the contour of this integration to imaginary energies, we actually deal with exponentially decreasing orbitals only. This applies also to the addition theorem, and a rapid convergence of the final energy integration is found

If the array under investigation is a regular lattice, we obtain an additional splitting of the electron dispersion function according to Bloch's theorem. The resulting final energy expression is obviously made up of the phase shift of the electron orbitals at the single atoms and of the interference of the scattering amplitudes caused by different atoms. A large phase shift factor and an additive interference of multiple scattering terms are necessary for obtaining large contributions to the total band energy. If the symmetry of the orbitals with energies close to the Fermi energy does not fit to the lattice structure considered, another lattice structure may have lower energy. Expression (31) enables an exact treatment of this important relationship between atomic potential, Fermi energy and lattice structure. A shift of the contour of integration to imaginary energies causes a smooth variation of the integrand and a rapid convergence of the integral. This reduces the sensitivity of the total band energy to variations of the band structure close to the Brillouin zone boundaries, which critically enters earlier investigations (Heine 1969).

Each explicit calculation into band energies and lattice structures on the basis of the present one-electron formalism may be supplemented by equivalent investigations into many-electron contributions. The above mathematical procedure was first used in investigations into these many-electron or van der Waals contributions. It is possible to attribute the correlation of different electrons to a photon exchange mechanism and to treat the average photon field using Maxwell's equations.

The resulting electric and magnetic modes between the atoms can be expressed in terms of spherical Bessel functions. By shifting the frequency integration over the average photon energy to the imaginary axis, we obtain final expressions analogous to equations (30) or (42). Since Bose rather than Fermi statistics is used, we do not find oscillations of the total correlation energy with increasing separation of the atoms. Since the fields considered are vectors rather than scalars, we find a dependence of multiplet contributions on the angles enclosed by the interaction diagram.

We expect the one-electron contributions to the total lattice energy generally to dominate over the many-electron contributions. The latter are important if the atomic potential $V(r)$ is weak, so that the phase shift experienced by the one-electron orbitals is small. A simultaneous treatment of one-electron and many-electron terms by the presented analogous methods covers the full scale from metallic muffin-tin lattices to van der Waals lattices like those of rare gases.

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