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Electron-Phonon Interaction and Phonon Dispersion Relations Using the Augmented-Plane-Wave Method*

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A new version of the "Schrödinger method" for treating the electron-phonon matrix element is presented. Using the Schrödinger equation, the matrix element is transformed so as to obtain the first-order perturbed charge density of the valence electrons self-consistently as the sum of two parts. The first or "bound" part corresponds to the rigid movement of the valence charge density inside a volume V_0 (chosen for maximum convenience) in the unit cell with the ion core, while the second or "deformation" part represents the rest of the perturbation and may be calculated as the self-consistent response to a weak effective driving potential, called the residual potential, which does not contain the deep well near the core. The screened matrix element is obtained, and the relationship to Bardeen's method and to the more recent pseudopotential methods is discussed. A certain resemblance of the residual potential to the Heine-Abarenkov model potential is pointed out. Finally, the dynamical matrix is transformed without approximation to be written as the sum of an interaction between pseudoatoms and a deformation part. The advantages of such a recasting are discussed. Explicit expressions are derived based on the APW representation of the valence wave functions, since it is intended to apply the formalism to transition metals and other more complicated solids.

I. INTRODUCTION

THERE have in the last few years been several fundamental calculations[1–7] of the phonon dispersion curves for simple metals, i.e., metals for which the cores are small and the conduction electrons are free-electron-like over most of the crystal volume. As is well known, this involves two central problems, namely, the calculation of the electron-phonon matrix element, and the calculation of the many-body response of the conduction electrons. In general, these problems are rather closely intertwined. If one tries to calculate the electron-phonon matrix element (henceforth referred to as the EPME) directly, one runs into problems of accuracy in evaluation of the EPME as well as of convergence in performing the perturbation sums. There have been two basic approaches to overcome these problems.

One approach has been through the use of pseudopotentials[2–5] or model potentials[6,7] in the case of free-electron-like metals. The pseudopotential method is based specifically on a representation of the valence wave function in terms of orthogonalized plane waves (OPW's), and relies on certain cancellations which occur between different terms when the EPME is expanded in terms of these functions, so that one may start with a basis set of single plane waves to represent the pseudo-wave-functions and calculate the effect of the lattice by ordinary second-order perturbation theory. The model potential of Heine and Abarenkov[8] (hereafter referred to as the HA potential), although not specifically based on the OPW scheme, also utilizes the above approach. However, calculations of phonon dispersion curves in metals using the OPW-based pseudopotential[2–5,9–11] so far have not been very successful in obtaining good agreement with experiment, except for Sham's calculations on sodium, which give reasonable agreement except for one branch. It should be noted that Sham uses a Born-Oppenheimer expansion rather than a simple perturbation expansion, and takes the bound motion of the core parts of the wave functions into account in detail. The HA potential gives better agreement, especially for potassium[6] but for other metals still contains discrepancies for several branches of the dispersion curves.

We believe that one reason why great accuracy is hard to achieve by these methods is the considerable cancellation that occurs between two contributions to the dynamical matrix (DM)—that due to the purely electrostatic interaction between the ions, and the band-structure contribution, i.e., that due to the second-order perturbation of the electron energies due to the lattice vibrations. Thus a small error in calculating the latter leads to a large error in the sum. Other reasons for the poor accuracy obtained in many cases include the fact that the band-structure contribution is expressed completely as a sum in reciprocal space which does not converge very rapidly,[4,7] and the fact that the OPW-based pseudopotential is sensitive to the details of the

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[9] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

[10] V. Heine and A. O. E. Animalu, Phil. Mag. **12**, 1249 (1965).

[11] V. C. Sahni, G. Venkataraman, and A. P. Roy, Phys. Letters **23**, 633 (1966). See also J. U. Koppel and A. A. Maradudin, *ibid.* **24A**, 244 (1967).

ionic potential near the cores and to the energies of the core states. The last disadvantage does not apply to the HA potential, although in that method the energy dependence of the potential is usually neglected. Perhaps the chief limitation of the above methods, however, is the fact that they cannot be applied to other than free-electron-like metals, such as the transition or rare-earth metals, or to tightly bound solids. This is obviously true of the OPW-based pseudopotential. It is possible that the HA model potential could be applied to these substances, but the theory would have to be modified, in the sense that one could no longer apply simple perturbation theory using a plane-wave basis set; and further, the self-consistent response of the actual (rather than pseudo) wave function inside the characteristic radius of the HA potential would have to be evaluated more accurately.

Another approach, which has been called the "Schrödinger method,"[5] is of the kind first used by Mott and Jones.[12] The Schrödinger equation is used to transform the integrals over the unit cell appearing in the EPME into surface integrals involving wave functions at the cell boundary, together with certain terms proportional to $(E_k-E_{k'})$, where k, k' refer to the initial and final states in the EPME, respectively. This transformation can actually be made in several different ways. The Mott and Jones transformation was utilized by Bardeen[13] in his pioneer calculation of the EPME in monovalent metals, taking electron screening into account. Toya[1] later extended Bardeen's method to calculate phonon dispersion relations for a number of metals. The Bardeen method, however, suffers from a number of defects. It assumes simple Wigner-Seitz wave functions for the conduction electrons which Taylor, Moore, and Vosko[14] have shown to be a fairly bad approximation even for simple metals. It also assumes that the potential in a unit cell is simply that due to the ion core in that cell together with the Hartree potential due to a uniform charge density in the cell, and it also approximates the Wigner-Seitz cell by a sphere. Further, Bardeen's calculation is not truly self-consistent, as has been pointed out by Cochran[15] and Sham,[2] in that he neglects the terms proportional to $(E_k-E_{k'})$ in the EPME *before* performing his self-consistency calculation, whereas both the electronic density perturbation and the energy perturbation involve virtual transitions for which $(E_k-E_{k'})$ is nonzero, and which will therefore contribute to both the screening and the dynamical matrix. It will be shown in Sec. IV that only for completely free electrons is Bardeen's result correct, so that caution must be exercised in applying it to most metals. The calculation also suffers from the same disadvantage mentioned in connection with the pseudopotential methods—namely the large cancellation between the electrostatic contribution to the DM, and the band-structure or electronic contribution.

Recently, Taylor, Moore, and Vosko[14] (henceforth referred to as TMV) have developed another version of the Schrödinger method and applied it to a calculation of the EPME in sodium, although they have not extended their method to the problem of calculating phonon dispersion curves. The chief advantage of the Schrödinger method lies in the fact that one is not restricted to free-electron metals. By transforming to an integral over the surface of the cell one eliminates in principle a large part of the difficulties associated with both the deep potential well near the cores as well as the atomiclike oscillations in the wave function in this region. However, TMV have pointed out that the surface integrals are extremely sensitive to the derivatives of the wave functions at the cell boundary and to the energies E_k of the unperturbed states, and thus in a sense the EPME calculated by this method is still implicitly dependent on the details of the potential inside the unit cell. However, with the advent of accurate solutions of the Schrödinger equation in a large number of crystals by modern computing techniques, it is likely that this Schrödinger method will be relied upon increasingly for accurate first-principles calculations of the EPME for many metals.

We finally point out another difficulty that has been present in calculations of the phonon frequencies in metals such as the noble or transition metals. The valence electrons are usually split up into s electrons and the latter are treated as atomiclike wave functions moving rigidly with the cores, and giving rise to an extra contribution to the DM in addition to the electrostatic and band-structure contributions. This is supposed to arise from overlap of the atomic orbitals representing the d electrons, and is usually parametrized according to the Born-Mayer type of potential.[16] Since such interactions are considered to be quite large, agreement with experiment may often be obtained by adjusting these parameters,[1,17] not withstanding the fact that the above picture of Born-Mayer interactions between overlapping atomic orbitals is not at all rigorously based. This has already been pointed out by Vosko[18] in connection with sodium. Strictly speaking, according to recent band-structure calculations for these metals[19] the s and d electrons should all be treated on the same footing, and any short-range interaction between the ion cores should arise in a natural way out of performing a systematic

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[19] T. Loucks, *Augmented Plane Wave Method* (W. A. Benjamin, Inc., New York, 1967), pp. 10, 11.

Born-Oppenheimer perturbation expansion to second order.

It is our purpose in this paper to present an alternative version of the Schrödinger method which appears to have several advantages in dealing with the difficulties that arise in the pseudopotential methods and at the same time does not suffer from the defects of the Bardeen method. It is based on the fact that during a lattice vibration, each core may be regarded as carrying in some sense a bound portion of the valence charge density rigidly along with it, so that the first-order perturbed charge density $\Delta\rho(\mathbf{r})$ may be split up into a bound part and a deformation part which represents the rest of the perturbation. Using Schrödinger's equation to transform the EPME, we find that it is precisely the terms proportional to $(E_k-E_{k'})$ in our method that give rise to the bound part of $\Delta\rho(\mathbf{r})$, and further that these terms arise mainly from the deep potential wells near the cores. Thus we are able to set up a truly self-consistent equation for the deformation part of $\Delta\rho(\mathbf{r})$ which turns out to be the self-consistent response to a weak residual potential, so that we may term our method the residual potential method. The above considerations remain true whether the electrons are free-electron-like or tightly bound, as we shall see. In Sec. II we show, by considering the case of a free atom, how separating out the bound part of $\Delta\rho(\mathbf{r})$ improves the convergence of the perturbation sums in the Born-Oppenheimer perturbation expansion and gives rise to explicit cancellation in the expression for the perturbed electron energies. Thus we may understand why the Born-Oppenheimer expansion converges, and why the phonon energies are small compared to the electronic energies, even though the perturbing potentials are very large in the regions of the cores. In Sec. III we develop the formalism in detail for an actual crystal. In Sec. IV we obtain and discuss the expression for the effective EPME. In Sec. V we use our formalism to develop an important transformation of the expression for the second-order energy perturbation to yield finally an explicit expression for the DM which contains two contributions. The first is due to interaction between rigid units composed essentially of the cores and the bound part of $\Delta\rho(\mathbf{r})$ surrounding each core, and may be expressed in terms of the usual force constant formalism.[20] The point to note is that the electrostatic interaction is now considerably reduced because of the compensation of the core charge by the bound part of $\Delta\rho(\mathbf{r})$. Thus the cancellation between the electrostatic and band-structure contributions in previous theories is explicitly built into our formalism without involving the matrix elements of our residual potential or the dielectric response function. The latter only go into calculating the second or deformation part of the DM which is much smaller than the conventional band-structure contribution, and hence errors in such calculations are not so critical. The rigid-atom force constants obtained in this way also contain a small non-Coulomb contribution due to exchange and correlation effects, which decreases rapidly with increasing neighbor distance. It should be pointed out that a model approximately along these lines was discussed earlier by Toya.[21]

We provide in Appendix A explicit formulas for some of the matrix elements that appear in our formalism based on the augmented-plane-wave (APW) representation of the crystal wave functions. The formalism may thus be applied to any solid for which an accurate APW band-structure calculation may be performed. Of course applying the formalism to a transition metal will still be far more complicated than applying it to a free-electron metal because of the unavoidable fact that the dielectric screening itself is very much more complicated in such solids. However, as we shall see in Sec. IV, our formalism will have helped considerably to simplify even this problem.

II. PHYSICAL BASIS OF THE METHOD

Let us first consider the case of an isolated hydrogen atom situated at the origin, and consider the electron to be in some state with wave function $\phi_m(\mathbf{r})$. Now consider a small displacement $\mathbf{u}$ of the nucleus. If $V(\mathbf{r})$ is the potential field of the undisplaced nucleus, the change in potential to first order in $\mathbf{u}$ is $-\nabla V(\mathbf{r})\cdot\mathbf{u}$. By Born-Oppenheimer perturbation theory, the first-order change in the wave function will be

$$\Delta\phi_m(\mathbf{r})=-\sum_\alpha u_\alpha \sum_{m'\neq m}\frac{\langle\phi_{m'}|\partial V/\partial x_\alpha|\phi_m\rangle}{E_m-E_{m'}}\phi_{m'}(\mathbf{r}),\quad (1)$$

where $E_{m'}$ denotes the unperturbed energy of state $\phi_{m'}$. If we write the Hamiltonian H as $P^2/2m+V(\mathbf{r})$, then we have the identity

$$\frac{\partial V}{\partial x_\alpha}=\left[\frac{\partial}{\partial x_\alpha},H\right].\quad (2)$$

Substituting in Eq. (1) and using the completeness property of the $\phi_{m'}$ we get

$$\begin{aligned}\Delta\phi_{m'}(\mathbf{r})&=-\sum_\alpha u_\alpha\sum_{m'\neq m}\langle\phi_{m'}|\frac{\partial}{\partial x_\alpha}|\phi_m\rangle\phi_{m'}(\mathbf{r})\\&=-\nabla\phi_m(\mathbf{r})\cdot\mathbf{u}.\end{aligned}\quad (3)$$

The change in electronic energy to second order in $\mathbf{u}$ is given by

$$\Delta E^{(2)}=\sum_{\alpha\beta}\left\{\sum_{m'\neq m}\frac{\langle\phi_m|\partial V/\partial x_\alpha|\phi_{m'}\rangle\langle\phi_{m'}|\partial V/\partial x_\beta|\phi_m\rangle}{E_m-E_{m'}}+\tfrac{1}{2}\langle\phi_m|\frac{\partial^2V}{\partial x_\alpha\partial x_\beta}|\phi_m\rangle\right\}u_\alpha u_\beta,\quad (4)$$

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[20] A. Maradudin, E. W. Montroll, and G. H. Weiss, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1963), Suppl. 3.

[21] T. Toya, *Lattice Dynamics* (Pergamon Press, Inc., New York, 1965), p. 91.

where we have noted that $\langle\phi_m|\partial V/\partial x_\alpha|\phi_m\rangle$ vanishes by Eq. (2). Using Eq. (2) and the completeness property of the $\phi_{m'}$, we may show also that

$$\Delta E^{(2)}=0. \quad (5)$$

The results in Eqs. (3) and (5) are physically obvious and could have been written down without recourse to perturbation theory. On the other hand if we had wished to calculate $\Delta\phi_m(\mathbf{r})$ using the actual perturbation sum in Eq. (1), we would have found it slowly convergent due to the deep potential well in $V(\mathbf{r})$ and the oscillations in $\phi_{m'}(\mathbf{r})$. Thus we see how we may allow for the effect of the deep potential well exactly in this case. The Born-Oppenheimer perturbation expansion ensures correct calculation of any quantity that can be usefully expanded in powers of $\mathbf{u}$, and the harmonic and adiabatic approximations of lattice dynamics imply that the energy perturbation due to the lattice vibrations is just such a quantity. Further, we see how, although the matrix elements $\langle\phi_m|\partial V/\partial x_\alpha|\phi_{m'}\rangle$ are not necessarily small, the two terms in Eq. (4) cancel each other. In the next section we generalize the above considerations to make a self-consistent perturbation expansion in an actual crystal lattice.

III. CALCULATION OF THE SELF-CONSISTENT ELECTRON RESPONSE

Let us consider a monatomic lattice, and in the usual manner split the electrons up into core electrons and valence electrons. For transition metals, we must place both *s* and *d* electrons in the latter category. For a phonon mode propagating with wave vector $\mathbf{q}$, one can write the lattice displacements as

$$u_\alpha{}^l=(N\Omega)^{-1/2}(Q_\mathbf{q}e^{i\mathbf{q}\cdot\mathbf{r}_l}+Q_\mathbf{q}{}^*e^{-i\mathbf{q}\cdot\mathbf{r}_l})e_\alpha, \quad (6)$$

where N is the number of unit cells per unit volume, Ω is the total crystal volume, $Q_\mathbf{q}$ is the normal coordinate operator, $\mathbf{r}_l$ is the equilibrium position of the nucleus in the lth cell, and e_α is a Cartesian component of the unit polarization vector, which we can take to be real in this case. Let us choose a volume V_0 inside each unit cell (which we leave arbitrary for the moment), and write the perturbed electron density to first order as

$$\Delta\rho(\mathbf{r})=\Delta\rho^{(0)}(\mathbf{r})+\Delta\rho^{(1)}(\mathbf{r}), \quad (7)$$

where we define

$$\Delta\rho^{(0)}(\mathbf{r})=-\sum_{l\alpha}\frac{\partial}{\partial x_\alpha}\rho(\mathbf{r}-\mathbf{r}_l)u_\alpha{}^l. \quad (8)$$

$\rho(\mathbf{r}-\mathbf{r}_l)$ is defined as that function which is equal to the unperturbed valence number density for $\mathbf{r}$ inside the volume V_0 in the lth cell and is zero for $\mathbf{r}$ outside it. The fact that $\Delta\rho^{(0)}(\mathbf{r})$ is not defined on the surface of V_0 need not concern us for reasons discussed below. Thus $\Delta\rho^{(0)}(\mathbf{r})$ represents to first order in the $\mathbf{u}^l$, the rigid movement of the unperturbed number density inside V_0 with the core in that unit cell. We may term it the bound part of $\Delta\rho(\mathbf{r})$. The second term $\Delta\rho^{(1)}(\mathbf{r})$ then represents all the rest of the perturbation and we call it the deformation part.

We assume that the bare interaction between valence electrons that goes into a self-consistent screening calculation may be written in terms of a local potential $v(\mathbf{r}-\mathbf{r}')$. Its Fourier transform is assumed to be of the form

$$v(\mathbf{K})=(4\pi e^2/\Omega K^2)[1-f(\mathbf{K})], \quad (9)$$

where $f(\mathbf{K})$ is supposed to allow approximately for exchange and correlation effects. There are several choices for the form of $f(\mathbf{K})$. We may follow Sham[2] and Animalu[7] in taking $f(\mathbf{K})$ to be of the form

$$f(\mathbf{K})=\tfrac{1}{2}K^2/(K^2+\xi^2), \quad (10)$$

where ξ is the length of some characteristic wave vector which we may leave as an undetermined parameter since theoretical many-body calculations[22] which support the form (10) differ in estimates of ξ, and furthermore only apply to the case of a free-electron gas. The procedure of representing the exchange and correlation effects by a local potential in the above sense may be questioned. Nevertheless, practically all calculations of electron screening in real solids have eventually made this or an equivalent approximation.

Let $\phi_b(\mathbf{r}-\mathbf{r}_l)$ denote the potential seen by an electron due to the bare core at $\mathbf{r}_l$, and $\phi_t(\mathbf{r}-\mathbf{r}_l)$ that due to the core plus the unperturbed valence charge density inside volume V_0 surrounding it. We may term this composite unit a "pseudoatom" for our purposes. We have

$$\phi_t(\mathbf{r}-\mathbf{r}_l)=\phi_b(\mathbf{r}-\mathbf{r}_l)+\int_{V_0(l)}d\mathbf{r}'\,\rho(\mathbf{r}'-\mathbf{r}_l)v(\mathbf{r}-\mathbf{r}'), \quad (11)$$

where the suffix $V_0(l)$ indicates integration over the volume V_0 in the lth cell only. If the unperturbed crystal potential is $V(\mathbf{r})$, we may split $\phi_t(\mathbf{r}-\mathbf{r}_l)$ into two parts as

$$\phi_t(\mathbf{r}-\mathbf{r}_l)=W(\mathbf{r}-\mathbf{r}_l)+U(\mathbf{r}-\mathbf{r}_l), \quad (12)$$

where

$$\begin{aligned}W(\mathbf{r}-\mathbf{r}_l)&=\phi_t(\mathbf{r}-\mathbf{r}_l)-V(\mathbf{r}), &&\text{for } \mathbf{r} \text{ inside } V_0(l)\\ &=\phi_t(\mathbf{r}-\mathbf{r}_l), &&\text{for } \mathbf{r} \text{ outside } V_0(l) \quad (13)\end{aligned}$$

and

$$\begin{aligned}U(\mathbf{r}-\mathbf{r}_l)&=V(\mathbf{r}), &&\text{for } \mathbf{r} \text{ inside } V_0(l)\\ &=0, &&\text{for } \mathbf{r} \text{ outside } V_0(l). \quad (14)\end{aligned}$$

Physically, $W(\mathbf{r}-\mathbf{r}_l)$ is a potential which for $\mathbf{r}$ outside $V_0(l)$ is due to the pseudoatom inside $V_0(l)$, and for $\mathbf{r}$ inside $V_0(l)$ is equal to *minus* that due to all the charge distribution outside $V_0(l)$. Its general form is illustrated in Fig. 1. The deep potential well in the core region is incorporated into the second term of Eq. (12).

Note that the apparent singularities in the deriva-

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[22] S. H. Vosko and D. J. W. Geldart (to be published). See also R. H. Ritchie and J. Crowell, Bull. Am. Phys. Soc. **11**, 533 (1966).

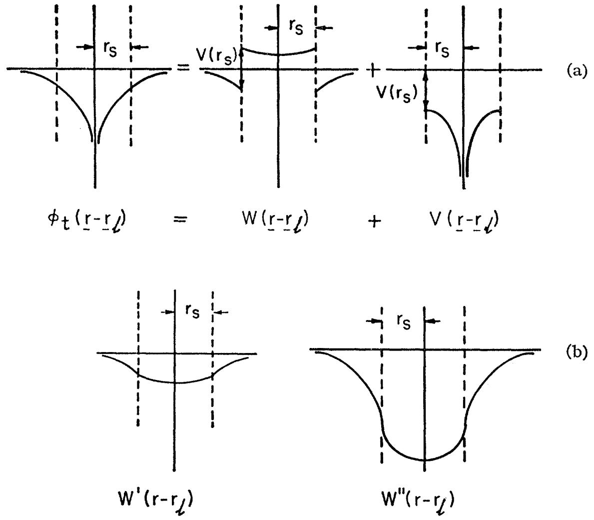

FIG. 1. (a) Illustration of the way the potential due to a pseudoatom is split up. (b) General form of the potentials W' and W'' defined in the text.

tives of W and U due to their discontinuity on the surface of V_0 cancel out since their sum is continuous. The sum of $\Delta\rho^{(0)}$ and $\Delta\rho^{(1)}$ is also continuous across this boundary. We may thus exclude all the boundaries of the volumes V_0 by enclosing their surfaces between shells $(S_0-\epsilon)$ and $(S_0+\epsilon)$. By letting $\epsilon\rightarrow 0$ we can let the excluded volumes tend to zero eventually, in which case so will their contribution to the matrix elements, to $\Delta\rho(\mathbf{r})$, and to the energy perturbation, since these all involve quantities which are continuous across the boundary. Hence by "the volume V_0" we shall always mean the limiting volume which tends to V_0 from *inside*, and similarly by "the surface S_0" we shall mean the surface which tends to the surface of our chosen V_0 from inside.

In order to calculate $\Delta\rho(\mathbf{r})$ we use first-order self-consistent Born-Oppenheimer perturbation theory

$$\Delta\psi_k=\sum_{k'}{}'\frac{\langle\psi_{k'}|\Delta V_t|\psi_k\rangle}{E_k-E_{k'}}\psi_{k'}\,, \tag{15}$$

where the prime over the summation indicates that we omit the term $k'=k$, and ΔV_t is the *total* self-consistent perturbation due to the phonon to first order in the lattice displacements.

$$\Delta V_t(\mathbf{r})=\sum_{l,\alpha}\frac{\partial}{\partial R_\alpha{}^l}\phi_b(\mathbf{r}-\mathbf{r}_l)u_\alpha{}^l+\int d\mathbf{r}'\,\Delta\rho^{(0)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')+\int d\mathbf{r}'\,\Delta\rho^{(1)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')\,, \tag{16}$$

where $\partial/\partial R_\alpha{}^l$ denotes differentiation with respect to the instantaneous nuclear coordinate $\mathbf{R}^l$. Using the definitions (8) and (11) we can lump the first two terms together to obtain

$$\Delta V_t(\mathbf{r})=-\sum_{l,\alpha}u_\alpha{}^l\frac{\partial}{\partial x_\alpha}\phi_t(\mathbf{r}-\mathbf{r}_l)+\int d\mathbf{r}'\,\Delta\rho^{(1)}(\mathbf{r}-\mathbf{r}')v(\mathbf{r}-\mathbf{r}')\,. \tag{17}$$

For most purposes we shall find it convenient to take V_0 to be a sphere of some radius r_s centered about $\mathbf{r}_l$ and we shall assume that it is chosen small enough so that $\rho(\mathbf{r}-\mathbf{r}_l)$ is spherically symmetric about $\mathbf{r}_l$. (This is in practice not too stringent a restriction on r_s.)

$$\Delta V_t(\mathbf{r})=\Delta V^{\mathrm{I}}(\mathbf{r})+\Delta V^{\mathrm{II}}(\mathbf{r})+\Delta V^{\mathrm{III}}(\mathbf{r})\,, \tag{18}$$

where

$$\Delta V^{\mathrm{I}}(\mathbf{r})=-\sum_{l,\alpha}u_\alpha{}^l\frac{\partial}{\partial x_\alpha}W(\mathbf{r}-\mathbf{r}_l)\,, \tag{19}$$

$$\Delta V^{\mathrm{II}}(\mathbf{r})=\int d\mathbf{r}'\,\Delta\rho^{(1)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}')\,, \tag{20}$$

$$\begin{aligned}\Delta V^{\mathrm{III}}(\mathbf{r})&=-u_\alpha{}^l\frac{\partial V(\mathbf{r})}{\partial x_\alpha}\,,\quad\text{for } \mathbf{r} \text{ inside } V_0(l)\\&=0\,,\qquad\qquad\text{for } \mathbf{r} \text{ outside all the } V_0(l).\end{aligned} \tag{21}$$

The removal of the singularity in the derivative of $W(\mathbf{r}-\mathbf{r}_l)$ at the surface of $V_0(l)$ by means of our limiting process has some important effects when we calculate the Fourier transform of $\Delta V^{\mathrm{I}}(\mathbf{r})$.

Let us define the Fourier transform of any potential $V(\mathbf{r})$ by

$$V(\mathbf{K})=\frac{1}{\Omega}\int d\mathbf{r}\,V(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}. \tag{22}$$

Then we may split up the integral into two parts corresponding to the region inside V_0 and that outside it. Thus

$$\begin{aligned}&\frac{1}{\Omega}\sum_\alpha u_\alpha{}^l\int d\mathbf{r}\frac{\partial}{\partial x_\alpha}W(\mathbf{r}-\mathbf{r}_l)e^{-i\mathbf{K}\cdot\mathbf{r}}\\&=\frac{1}{\Omega}e^{-i\mathbf{K}\cdot\mathbf{r}_l}\sum_\alpha u_\alpha{}^l\left\{\int_{V_0(l)}d\mathbf{r}\frac{\partial W}{\partial x_\alpha}(\mathbf{r}-\mathbf{r}_l)e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)}+\int_{\mathbf{r}\text{ outside }V_0(l)}d\mathbf{r}\frac{\partial W}{\partial x_\alpha}(\mathbf{r}-\mathbf{r}_l)e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)}\right\}\\&=\frac{1}{\Omega}e^{-i\mathbf{K}\cdot\mathbf{r}_l}\sum_\alpha u_\alpha{}^l\left\{iK_\alpha\int_{\text{all space}}d\mathbf{r}\,W(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}-\int_{S_0}dS_\alpha\,V(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}}\right\},\end{aligned} \tag{23}$$

where we have used the divergence theorem on the integrals inside and outside V_0. The resulting surface integral contains the difference between the values that $W(\mathbf{r})$ tends to at the surface of V_0 from inside and outside, respectively, and by the definition of $W(\mathbf{r})$ in terms of Eq. (13), this is simply $V(\mathbf{r})$. We shall further assume that $V(\mathbf{r})$ may be taken to be spherically symmetric on the surface S_0 and equal to $V(r_s)$ everywhere. We may then transform the surface integral in Eq. (23) back into a volume integral to obtain

$$\frac{1}{\Omega}\sum_{\alpha} u_\alpha{}^l \int d\mathbf{r}\,\frac{\partial W}{\partial x_\alpha}(\mathbf{r}-\mathbf{r}_l)e^{-i\mathbf{K}\cdot\mathbf{r}} = ie^{-i\mathbf{K}\cdot\mathbf{r}_l}\sum_{\alpha} u_\alpha{}^l K_\alpha W'(\mathbf{K}), \tag{24}$$

where

$$W'(\mathbf{K})=\frac{1}{\Omega}\int_{\text{all space}} d\mathbf{r}\,W(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}} +\frac{1}{\Omega}V(r_s)\int_{V_0} d\mathbf{r}\,e^{-i\mathbf{K}\cdot\mathbf{r}}. \tag{25}$$

It is the transform of the potential $W'(\mathbf{r})$ given by

$$\begin{aligned} W'(\mathbf{r})&=\phi_t(\mathbf{r})-V(\mathbf{r})+V(\mathbf{r}_s), && \text{for } \mathbf{r} \text{ inside } V_0\\ &=\phi_t(\mathbf{r}), && \text{for } \mathbf{r} \text{ outside } V_0. \end{aligned} \tag{26}$$

This potential is also illustrated in Fig. 1. It may be noticed that unlike $W(\mathbf{r})$ it does not possess a discontinuity at r_s. Its derivatives are discontinuous at r_s but this discontinuity is small because the gradient of $V(\mathbf{r})$ at r_s will in general be small. Thus $W'(\mathbf{K})$ may in general be expected to decrease rapidly with increasing $\mathbf{K}$. An explicit expression for $W'(\mathbf{K})$ may be obtained from Eqs. (26).

$$W'(\mathbf{K})=W(\mathbf{K})+(V_0/\Omega)V(r_s)\mathcal{G}(Kr_s), \tag{27}$$

where

$$W(\mathbf{K})=\frac{1}{\Omega}\int_{\text{all space}} d\mathbf{r}\,W(\mathbf{r})e^{-i\mathbf{K}\cdot\mathbf{r}} \tag{28a}$$

and

$$\mathcal{G}(x)=3\left(\frac{x\cos x-\sin x}{x^3}\right). \tag{28b}$$

By means of Eqs. (6) and (24) we may immediately write down the transform of ΔV^{I} as

$$\Delta V^{\mathrm{I}}(\mathbf{K})=-(N\Omega)^{1/2}i\Big(\sum_{\alpha} e_\alpha K_\alpha\Big) \times W'(\mathbf{K})\sum_{H}\left[Q_{\mathbf{q}}\delta_{\mathbf{K},\mathbf{q}+\mathbf{H}}+Q_{\mathbf{q}}{}^*\delta_{-\mathbf{K},\mathbf{q}+\mathbf{H}}\right]$$

$$[\mathbf{H}=\text{a reciprocal lattice vector}]. \tag{29}$$

Also from Eq. (20),

$$\Delta V^{\mathrm{II}}(\mathbf{K})=\Omega\Delta\rho^{(1)}(\mathbf{K})v(\mathbf{K}). \tag{30}$$

Let us calculate the matrix elements of $\Delta V^{\mathrm{III}}(\mathbf{r})$ which contain the deep potential wells due to the cores.

$$\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle=-\sum_{l,\alpha} u_\alpha{}^l\int_{V_0(l)} d\mathbf{r}\,\psi_{k'}{}^*\frac{\partial V}{\partial x_\alpha}\psi_k. \tag{31}$$

We may now again use the identity represented by Eq. (2), except that we have to allow for H being non-Hermitian in the finite volume V_0. Therefore we write

$$\begin{aligned} \psi_{k'}{}^*\frac{\partial V}{\partial x_\alpha}\psi_k&=\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}H\psi_k-\psi_{k'}{}^*H\frac{\partial}{\partial x_\alpha}\psi_k\\ &=(E_k-E_{k'})\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k\\ &\quad-\frac{\hbar^2}{2m}\left\{\nabla^2\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k-\psi_{k'}{}^*\nabla^2\frac{\partial}{\partial x_\alpha}\psi_k\right\}, \end{aligned}$$

where we have used the Schrödinger equation for ψ_k and $\psi_{k'}$. Substituting in Eq. (31), we get

$$\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle =-\sum_{l,\alpha} u_\alpha{}^l(E_k-E_{k'})\int_{V_0(l)} d\mathbf{r}\,\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k+M_{k'k}, \tag{32}$$

where

$$M_{k'k}=\frac{\hbar^2}{2m}\sum_{l,\alpha} u_\alpha{}^l\int_{V_0(l)} d\mathbf{r} \times\left\{\nabla^2\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k-\psi_{k'}{}^*\nabla^2\frac{\partial}{\partial x_\alpha}\psi_k\right\}. \tag{33a}$$

Using Green's theorem, this can also be written as

$$M_{k'k}=\frac{\hbar^2}{2m}\sum_{l,\alpha} u_\alpha{}^l\int_{S_0(l)} dS \times\left\{\frac{\partial}{\partial n}\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k-\psi_{k'}{}^*\frac{\partial^2}{\partial n\partial x_\alpha}\psi_k\right\}, \tag{33b}$$

where $\partial/\partial n$ denotes differentiation normal to the surface $S_0(l)$. Using the result in Eq. (32), we get from Eq. (15)

$$\Delta\psi_k(\mathbf{r})={\sum_{k'}}'\left\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle+M_{k'k}\right\}\frac{\psi_{k'}(\mathbf{r})}{E_k-E_{k'}} -{\sum_{k'}}'\sum_{l,\alpha} u_\alpha{}^l\psi_{k'}(\mathbf{r})\int_{V_0(l)} d\mathbf{r}'\,\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha{}'}\psi_k. \tag{34}$$

In the second term we may formally include the term $k'=k$ since it vanishes for finite $\mathbf{q}$ by Bloch's theorem. We may then use the completeness property of the $\psi_{k'}$ to do the sum in the last term, to obtain

$$\Delta\psi_k(\mathbf{r})={\sum_{k'}}'\left\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle+M_{k'k}\right\}\frac{\psi_{k'}(\mathbf{r})}{E_k-E_{k'}} -\sum_{l,\alpha} u_\alpha{}^l\frac{\partial}{\partial x_\alpha}\psi_k(\mathbf{r})\gamma(\mathbf{r}-\mathbf{r}_l), \tag{35}$$

where

$$\gamma(\mathbf{r}-\mathbf{r}_l)=1\,,\quad \text{for } \mathbf{r} \text{ inside } V_0(l)$$
$$=0\,,\quad \text{for } \mathbf{r} \text{ outside } V_0(l). \tag{36}$$

Note that Eq. (35) does not imply any discontinuity in $\Delta\psi_k$ on the surfaces S_0 since the first term will cancel out any discontinuity in the second.

In Appendix B, it is proved that Eq. (35) leads to an expression for $\Delta\rho(\mathbf{r})$ which is exactly of the form assumed in Eq. (7), with the deformation part $\Delta\rho^{(1)}(\mathbf{r})$ given by[23]

$$\Delta\rho^{(1)}=\sum_{k,k'}{}' \frac{n(k)-n(k')}{E_k-E_{k'}} \times\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle+M_{k'k}\}\psi_k{}^*\psi_{k'}. \tag{37}$$

Since ΔV^{II} also involves $\Delta\rho^{(1)}(\mathbf{r})$ we have effectively a self-consistency equation for this quantity. It is convenient to write it in terms of its Fourier transform. It may be shown that the only nonvanishing Fourier components of $\Delta\rho^{(1)}$ are $\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})$ and $\Delta\rho^{(1)}[-(\mathbf{q}+\mathbf{H})]$, the latter being the complex conjugates of the former. Using Eq. (29) we obtain from Eq. (37),

$$\begin{aligned}\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H}) &=\sum_{\mathbf{H}'}{}' \Big\{v(\mathbf{q}+\mathbf{H}')\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H}') \\ &\quad -(N/\Omega)^{1/2}iQ_{\mathbf{q}}\sum_{\alpha}(\mathbf{q}+\mathbf{H}')_\alpha \\ &\quad \times e_\alpha W'(\mathbf{q}+\mathbf{H}')\Big\}\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}') \\ &\quad +\sum_{k,k'}{}' \frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}M_{k'k}\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle\,,\end{aligned} \tag{38}$$

where

$$\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')=\sum_{k,k'}{}' \frac{n(k)-n(k')}{E_k-E_{k'}} \times\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H}')\cdot\mathbf{r}}|\psi_k\rangle. \tag{39}$$

Equation (39) has the familiar form of a general self-consistent screening equation (see Sham and Ziman[24] or Animalu,[25] for example) where $\Delta\rho^{(1)}(\mathbf{r})$ is the self-consistent response to a driving potential whose matrix elements between ψ_k and $\psi_{k'}$ are given by

$$\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}|\psi_k\rangle+M_{k'k}\}.$$

The form in which the last term of Eq. (38) has been written means that we may treat the nonlocal part as effectively Hermitian. The non-Hermitian part is incorporated in $\Delta\rho^{(0)}$ as shown in Appendix B. As explained in the Introduction, we may refer to these matrix elements as the matrix elements of our "residual potential." By Eq. (29) we see that the first part corresponds to the movement of a local potential with form factor $W'(\mathbf{K})$, where the deep well near the core has been removed, and the second part corresponds to a nonlocal non-Hermitian effective potential acting between states ψ_k and $\psi_{k'}$. The analogies with ordinary pseudopotentials are obvious. Note that we do not need to assume for this purpose that there exists a weak pseudopotential for the static lattice. In fact for the limiting case of tightly bound nonoverlapping wave functions, it may be seen that if we choose V_0 to be the whole unit cell, the $M_{k'k}$ become very small by Eq. (33b) since the ψ_k are small on the cell surface, while $\langle\psi_{k'}|\Delta V^{\mathrm{I}}|\psi_k\rangle$ remains small. This is to be expected since in this case $\Delta\rho^{(0)}(\mathbf{r})$ will represent the major portion of $\Delta\rho(\mathbf{r})$ as is obvious physically. Note also that even outside V_0, $W(\mathbf{r})$ is much weaker than the Coulomb potential due to the bare ion because of the neutralizing charge inside V_0.

It may be seen that letting V_0 in the unit cell shrink to zero volume causes $\Delta\rho^{(0)}$ and $M_{k'k}$ to vanish by definition, and $W'(\mathbf{r})$ becomes the bare ionic potential, so that our residual potential goes over in this limit to the actual potential. The other extreme limit is to take V_0 to be the whole unit cell. However, because of the inconvenient geometry of the cell surface, one is forced to make the approximation of the equivalent Wigner-Seitz sphere, with consequent loss of accuracy in calculating $M_{k'k}$ because of its sensitivity to the derivatives of the wave functions at the surface of V_0. Further, our assumption of the spherical symmetry of $V(\mathbf{r})$ on this surface is liable to break down. Since we wish to emphasize the application of the APW method to our scheme, the natural choice for us will be to take V_0 to be the APW sphere in the unit cell. In Appendix A, we have explicitly derived an expression for $M_{k'k}$ using its representation in terms of a surface integral in Eq. (33b) and based on the APW method. It turns out to be calculable in terms of quantities which are calculated in the course of an ordinary APW calculation. The APW-based $M_{k'k}$ is likely to be particularly accurate, since by the nature of the APW method, the wave functions ψ_k *inside* V_0 are numerical solutions of the Schrödinger equation for the given energy E_k, which is really all that the rigorous derivation of Eq. (33) assumes, even if the finite number of APW's taken makes ψ_k only an approximate solution of the Schrödinger equation outside the volumes V_0. As mentioned previously, we may take V_0 as the limit of a sphere *tending* to the APW sphere from *inside*. For the same reason, any possible discontinuity in the slope of the ψ_k obtained by the APW method at the APW radius need not bother us. Note that the matrix elements of the residual potential do not involve the details of the ionic potential or the wave functions inside V_0 explicitly, although they might

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[23] The author is indebted to Dr. R. Pick for illuminating discussions on this point.

[24] L. J. Sham and J. M. Ziman, Solid State Phys. **15**, 221 (1963).

[25] A. O. E. Animalu, Phil. Mag. **11**, 379 (1965).

be implicitly involved in the sense that they might affect the surface integral used to calculate $M_{k'k}$.

IV. DISCUSSION OF THE SCREENED ELECTRON-PHONON MATRIX ELEMENT

It may be verified that the formal solution to Eq. (38) is given by

$$\begin{aligned}\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})\\ =\frac{1}{v(\mathbf{q}+\mathbf{H})}\sum_{\mathbf{H}'}\Big[(N/\Omega)^{1/2}iQ_{\mathbf{q}}\sum_{\alpha}(\mathbf{q}+\mathbf{H}')_{\alpha}\\ \times e_{\alpha}W'(\mathbf{q}+\mathbf{H}')\{\delta_{\mathbf{HH}'}-\epsilon^{-1}(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')\}\\ +\frac{1}{\Omega}\epsilon^{-1}(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')v(\mathbf{q}+\mathbf{H}')\sum_{k,k'}{}'\frac{n(k)-n(k')}{E_k-E_{k'}}\\ \times\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H}')\cdot\mathbf{r}}|\psi_{k'}\rangle M_{k'k}\Big],\quad(40)\end{aligned}$$

where the dielectric matrix $\epsilon(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')$ is defined as[24]

$$\epsilon(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')=\delta_{\mathbf{HH}'}-v(\mathbf{q}+\mathbf{H})\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')\quad(41)$$

and $\chi(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')$ is defined in Eq. (39). In Eq. (40), we have taken account of the nonlocal and non-Hermitian nature of the residual potential, and exchange and correlation corrections to the Hartree screening approximately through the form of $v(\mathbf{K})$ given in Eq. (9). As is well known,[24] the real difficulty lies in inverting the matrix ϵ.

It is here that the simplicity in the treatment of free-electron metals is manifest, as ϵ collapses into the well-known scalar dielectric function for a free-electron gas. For more complicated solids, we may note that the ψ_k outside the volume V_0 in each cell are in general smooth combinations of a few plane waves. Since the major portion of the perturbed charge density inside the volume V_0 may be represented by $\Delta\rho^{(0)}(\mathbf{r})$, we might hope to get an accurate enough estimate of $\Delta\rho^{(1)}$ from Eq. (40) by calculating the dielectric matrix using simply the "smooth" parts of the linear combinations of the APW's analytically continued inside V_0. However, we shall undoubtedly still need several combinations of plane waves for this purpose, and these will give rise to off-diagonal elements in ϵ corresponding to "local field effects" which we may no longer neglect. Nevertheless our formalism has made the sum over $\mathbf{H}'$ in Eq. (40) much more convergent than if we had used the actual bare ionic potential to calculate $\Delta\rho(\mathbf{r})$ self-consistently. We may thus truncate the matrix $\epsilon(\mathbf{q}+\mathbf{H},\ \mathbf{q}+\mathbf{H}')$ to be of finite size, invert it and calculate $\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})$ from Eq. (40).

Now from Appendix A,

$$M_{k'k}=i(N/\Omega)^{1/2}[Q_{\mathbf{q}}\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}+Q_{\mathbf{q}}^{*}\Delta_{\mathbf{k}'-\mathbf{k},-\mathbf{q}}]\sum_{\alpha}e_{\alpha}I_{\alpha}^{k'k},$$

where the symbol $\Delta_{\mathbf{k}'-\mathbf{k};\mathbf{q}}$ denotes unity if $\mathbf{k}'-\mathbf{k}=\mathbf{q}$ modulus, a reciprocal lattice vector, and zero otherwise; $\mathbf{k},\mathbf{k}'$ denote the Bloch wave vectors of the states k,k', respectively, in the reduced zone scheme. Thus the state k is specified by $\mathbf{k}$ and a band index v. Using this form, we may for convenience write $\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})$ as

$$\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})=i(N/\Omega)^{1/2}Q_{\mathbf{q}}\sum_{\alpha}e_{\alpha}F_{\alpha}(\mathbf{q}+\mathbf{H}),\quad(42)$$

where

$$\begin{aligned}F_{\alpha}(\mathbf{q}+\mathbf{H})=\frac{1}{v(\mathbf{q}+\mathbf{H})}\sum_{H'}\Big[(\mathbf{q}+\mathbf{H}')_{\alpha}W'(\mathbf{q}+\mathbf{H}')\\ \times\{\delta_{\mathbf{HH}'}-\epsilon^{-1}(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')\}\\ +\epsilon^{-1}(\mathbf{q}+\mathbf{H},\mathbf{q}+\mathbf{H}')v(\mathbf{q}+\mathbf{H}')\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\\ \times\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H}')\cdot\mathbf{r}}|\psi_{k'}\rangle I_{\alpha}^{k'k}\Big].\quad(43)\end{aligned}$$

In terms of this we obtain for the total (screened) EPME, using Eqs. (29)–(31),

$$\begin{aligned}\langle\psi_{\kappa'}|\Delta V_t|\psi_{\kappa}\rangle=i(N/\Omega)^{1/2}Q_{\mathbf{q}}\sum_{\alpha}e_{\alpha}\\ \times\Big[I_{\alpha}^{\kappa'\kappa}+\Omega\sum_{\mathbf{H}}\{v(\mathbf{q}+\mathbf{H})F_{\alpha}(\mathbf{q}+\mathbf{H})\\ -(\mathbf{q}+\mathbf{H})_{\alpha}W'(\mathbf{q}+\mathbf{H})\}\langle\psi_{\kappa'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{\kappa}\rangle\\ +\frac{1}{N}i(E_{\kappa}-E_{\kappa'})\sum_{l}e^{i\mathbf{q}\cdot\mathbf{r}_l}\int_{V_0(l)}d\mathbf{r}\,\psi_{\kappa'}^{*}\frac{\partial}{\partial x_{\alpha}}\psi_{\kappa}\Big],\quad(44)\end{aligned}$$

where we have considered only the case where $\boldsymbol{\kappa}'=\boldsymbol{\kappa}+\mathbf{q}$ modulus a reciprocal lattice vector. In the case where $\boldsymbol{\kappa}'=\boldsymbol{\kappa}-\mathbf{q}$ modulus a reciprocal lattice vector may be obtained from the Hermitian property of the EPME. Since self-consistency has already been achieved, we may at this stage neglect the last term in Eq. (44) for energy conserving transitions. Note that neglecting it *before* the self-consistency calculation would have resulted in the neglect of the bound part $\Delta\rho^{(0)}$ altogether.

We now discuss the relationship between our method and Bardeen's original method.[13] This utilized the famous Mott and Jones identity which is effectively an alternative expression for $\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle$ in our terminology:

$$\begin{aligned}\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle=-\sum_{l,\alpha}u_{\alpha}^{l}(E_{k'}-E_k)\\ \times\int_{V_0(l)}d\mathbf{r}\frac{\partial}{\partial x_{\alpha}}(\psi_{k'}^{*}\psi_k)+M_{k'k}^{MJ},\quad(45)\end{aligned}$$

where

$$M_{k'k}{}^{MJ}=\frac{\hbar^2}{2m}\sum_{l,\alpha}u_\alpha{}^l\int_{S_0(l)}dS \times\left\{\frac{\partial}{\partial n}\psi_k\frac{\partial}{\partial x_\alpha}\psi_{k'}{}^*-\psi_k\frac{\partial^2}{\partial n\partial x_\alpha}\psi_{k'}{}^*\right\}. \quad (46)$$

A comparison of Eqs. (45) and (46) with Eqs. (32) and (33b) shows that $M_{k'k}{}^{MJ}$ is actually the Hermitian conjugate of our $M_{k'k}$, i.e., $M_{k'k}{}^{MJ}=M_{kk'}{}^*$, and that the terms proportional to $(E_k-E_{k'})$ are different in the two cases. Equations (32) and (45) in fact show that our residual potential is Hermitian only if it acts between two states of the same energy. This is in accord with the general behavior of pseudopotentials.[26]

As stated in the Introduction, Bardeen neglects the term involving $(E_k-E_{k'})$ at the outset. He further assumes plane waves for the ψ_k and parabolic energy bands, and is led to neglect also a part of $M_{k'k}{}^{MJ}$ equal to

$$(E_{k'}-E_k)\sum_{l,\alpha}u_\alpha{}^l\int_{V_0(l)}d\mathbf{r}\,\psi_k\frac{\partial}{\partial x_\alpha}\psi_{k'}{}^*.$$

Thus the sum of the neglected terms is equal to

$$(E_k-E_{k'})\sum_{l,\alpha}u_\alpha{}^l\int_{V_0(l)}d\mathbf{r}\,\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k,$$

which, apart from a sign, is just the first term of Eq. (32). This is only rigorously correct for a solid where the valence charge density is uniform everywhere, for then $\operatorname{grad}\rho(\mathbf{r})$ vanishes everywhere inside V_0. Bardeen's method will therefore be quite inaccurate if applied to other than free-electron metals.

It should be noted that TMV in their calculation of the screened EPME also drop a term proportional to $(E_k-E_{k'})$ *before* dividing by a dielectric function, although the neglected terms may be smaller in their case.

Finally, we point out a close similarity between our residual potential and the method of Animalu and Heine.[7,10] Let us consider the case where the wave functions may be described by single OPW's. In Appendix C we prove that a slightly different way of splitting $\Delta\rho$ into bound and deformation parts leads to a driving potential whose local part corresponds to the movement with each ion of a potential

$$\begin{aligned} W''(\mathbf{r})&=-(Z-Z'+Z'')e^2/r, \quad \text{for } r>r_s \\ &(r_s=\text{radius of sphere } V_0) \end{aligned} \quad (47)$$

where $+Ze$ is the core charge, $-Z'e$ is the total charge of the valence electron charge distribution inside V_0, and $-Z''e$ is the value the latter quantity would have if the valence charge density were everywhere equal to its surface value $\rho(r_s)$ inside V_0. We have assumed in deriving Eq. (47) that for $r>r_s$ there are no exchange or correlation corrections to the core potential. Note that $(Z-Z'+Z'')=Z^*$, the effective valence on the core which is different from Z due to the core part of the valence charge density. Figure 1 shows that for $r<r_s$, $W''(\mathbf{r})$ is small and slowly varying, so that its contribution to $\langle\psi_{k'}|\Delta\tilde{V}^{\mathrm{I}}|\psi_k\rangle$ is small. The driving potential also includes a nonlocal non-Hermitian part $M_{k'k}$ which is mainly determined by the ψ_k and their derivatives at r_s. In the method of Animalu and Heine, $\Delta\tilde{\rho}^{(0)}$ is effectively taken into account by letting the core parts of the valence wave functions move with the cores, and $\Delta\rho^{(1)}$ is the self-consistent response to a potential given by

$$\begin{aligned} V_M&=-Z^*e^2/r, \quad (r>r_s) \\ &=-\textstyle\sum_l A_lP_l, \quad (r<r_s) \end{aligned} \quad (48)$$

where A_lP_l is an operator acting on the lth angular momentum component of the wave function and again may be determined by the value of the wave function and its derivatives at r_s.

We note however that it is our particular transformation for $\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle$ in Eq. (33) which allows us to make the important transformation of the DM into a pseudoatom part and a deformation part as described in the next section.

V. DERIVATION OF THE DYNAMICAL MATRIX

Since we are treating only the tightly bound core electrons and the nuclei as the cores, we may suppose the latter to interact directly by means of a Coulomb potential $\phi^c(\mathbf{r})$. Then by the Born-Oppenheimer theorem, the potential energy function for the nuclear displacements is given by

$$\Phi^{(2)}=\tfrac{1}{2}\sum_{l,l',\alpha,\beta}(\phi_{\alpha\beta}{}^{ll'})^c u_\alpha{}^l u_\beta{}^{l'}+\Delta E^{(2)}, \quad (49)$$

where

$$\begin{aligned} (\phi_{\alpha\beta}{}^{ll'})^c&=-\left\{\frac{\partial^2\phi^c}{\partial x_\alpha\partial x_\beta}\right\}_{\mathbf{r}=\mathbf{r}_l-\mathbf{r}_{l'}}, \quad \text{for } l\neq l' \\ &=-\sum_{l'\neq l}(\phi_{\alpha\beta}{}^{ll'})^c, \quad \text{for } l=l' \end{aligned} \quad (50)$$

and $\Delta E^{(2)}$ is the energy perturbation for the valence electrons to second order in the displacements as calculated from self-consistent Born-Oppenheimer perturbation theory. It is given by[1,2]

$$\begin{aligned} \Delta E^{(2)}=\tfrac{1}{2}{\sum_{k,k'}}'\frac{n(k)}{E_k-E_{k'}} &\times\{\langle\psi_k|\Delta V_b{}^{(1)}|\psi_{k'}\rangle\langle\psi_{k'}|\Delta V_t|\psi_k\rangle \\ &+\langle\psi_k|\Delta V_t|\psi_{k'}\rangle\langle\psi_{k'}|\Delta V_b{}^{(1)}|\psi_k\rangle\} \\ &+\sum_k n(k)\langle\psi_k|\Delta V_b{}^{(2)}|\psi_k\rangle, \end{aligned} \quad (51)$$

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[26] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

where

$$\Delta V_b^{(1)}(\mathbf{r})=\sum_{l,\alpha} u_\alpha^l \frac{\partial}{\partial R_\alpha^l}\phi_b(\mathbf{r}-\mathbf{r}_l) \qquad (52)$$

and is the first-order change in bare ionic potential; ΔV_t is the total self-consistent first-order change in potential defined in Eq. (16), and $\Delta V_b^{(2)}$ is the second-order change in bare ionic potential given by

$$\Delta V_b^{(2)}(\mathbf{r})=\tfrac{1}{2}\sum_{l,\alpha,\beta} u_\alpha^l u_\beta^{l'} \frac{\partial^2}{\partial x_\alpha \partial x_\beta}\phi_b(\mathbf{r}-\mathbf{r}_l). \qquad (53)$$

Using Eq. (15), we may readily rewrite $\Delta E^{(2)}$ as

$$\Delta E^{(2)}=\frac{1}{2}\int d\mathbf{r}\,\Delta V_b^{(1)}(\mathbf{r})\Delta\rho(\mathbf{r}) +\int d\mathbf{r}\,n^0(\mathbf{r})\Delta V_b^{(2)}(\mathbf{r}), \qquad (54)$$

where $n^0(\mathbf{r})$ is the unperturbed valence electron density *everywhere* [to distinguish it from $\rho(\mathbf{r})$].

Using Eqs. (11) and (12) we may rewrite Eq. (52) as

$$\Delta V_b^{(1)}(\mathbf{r})=-\sum_{l,\alpha} u_\alpha^l \left\{\frac{\partial}{\partial x_\alpha}U(\mathbf{r}-\mathbf{r}_l)+\frac{\partial}{\partial x_\alpha}W(\mathbf{r}-\mathbf{r}_l) -\int_{V_0(l)} d\mathbf{r}'\,\rho(\mathbf{r}'-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}v(\mathbf{r}-\mathbf{r}')\right\}. \qquad (55)$$

By the same kind of transformation which led from Eq. (16) to Eqs. (18) and (19), we may transform this to get

$$\Delta V_b^{(1)}(\mathbf{r})=\Delta V^{\mathrm{I}}(\mathbf{r})+\Delta V^{\mathrm{III}}(\mathbf{r})+\Delta V^{\mathrm{IV}}(\mathbf{r}), \qquad (56)$$

where ΔV^{I}, ΔV^{III} are defined in Eqs. (19) and (21), and

$$\Delta V^{\mathrm{IV}}(\mathbf{r})=\sum_{l,\alpha} u_\alpha^l \int_{V_0(l)} d\mathbf{r}'\,\rho(\mathbf{r}'-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}v(\mathbf{r}-\mathbf{r}'). \qquad (57)$$

It may be verified that its Fourier transform is given by

$$\Delta V^{\mathrm{IV}}(\mathbf{K})=i(N\Omega)^{1/2}\sum_{\alpha} e_\alpha K_\alpha v(\mathbf{K})\Omega\rho(\mathbf{K}) \times\sum_{\mathbf{H}}\left[Q_{\mathbf{q}}\delta_{\mathbf{K},\mathbf{q}+\mathbf{H}}+Q_{\mathbf{q}}^*\delta_{-\mathbf{K},\mathbf{q}+\mathbf{H}}\right], \qquad (58)$$

$$\rho(\mathbf{K})=\text{transform of }\rho(\mathbf{r}).$$

Using Eqs. (56) and (7) we may split up Eq. (54) as follows:

$$\Delta E^{(2)}=\Delta E^{\mathrm{I}}+\Delta E^{\mathrm{II}}+\Delta E^{\mathrm{III}}+\Delta E^{\mathrm{IV}}+\Delta E^{\mathrm{V}}, \qquad (59)$$

where

$$\Delta E^{\mathrm{I}}=\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{I}}(\mathbf{r})\Delta\rho^{(0)}(\mathbf{r}), \qquad (60a)$$

$$\Delta E^{\mathrm{II}}=\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{I}}(\mathbf{r})\Delta\rho^{(1)}(\mathbf{r}), \qquad (60b)$$

$$\Delta E^{\mathrm{III}}=\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{III}}(\mathbf{r})\Delta\rho^{(1)}(\mathbf{r}), \qquad (60c)$$

$$\Delta E^{\mathrm{IV}}=\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{IV}}(\mathbf{r})\Delta\rho^{(0)}(\mathbf{r}) +\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{IV}}(\mathbf{r})\Delta\rho^{(1)}(\mathbf{r}), \qquad (60d)$$

$$\Delta E^{\mathrm{V}}=\int d\mathbf{r}\,n^{(0)}(\mathbf{r})\Delta V_b^{(2)}(\mathbf{r}) +\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{III}}(\mathbf{r})\Delta\rho^{(0)}(\mathbf{r}). \qquad (60e)$$

These quantities are evaluated in Appendix D, where it is shown that

$$\Delta E^{\mathrm{I}}=-\tfrac{1}{2}\sum_{ll',\alpha\beta} u_\alpha^l u_\beta^{l'}\left\{\int_{V_0(l)} d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_{l'})\right\}, \qquad (61a)$$

$$\Delta E^{\mathrm{II}}=-\tfrac{1}{2}NQ_{\mathbf{q}}Q_{\mathbf{q}}^*\sum_{\alpha\beta} e_\alpha e_\beta \sum_{\mathbf{H}} (\mathbf{q}+\mathbf{H})_\alpha \Omega W'(\mathbf{q}+\mathbf{H})F_\beta(\mathbf{q}+\mathbf{H})+\text{comp. conj.}, \qquad (61b)$$

$$\begin{aligned}\Delta E^{\mathrm{III}}=&-\tfrac{1}{2}\sum_{ll',\alpha\beta} u_\alpha^l u_\beta^{l'}\left\{\int d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_{l'})\right\}\\ &+\Big[\tfrac{1}{2}i(N\Omega)^{1/2}\sum_{\mathbf{H}}\sum_{\alpha} (\mathbf{q}+\mathbf{H})_\alpha e_\alpha \rho(\mathbf{q}+\mathbf{H})v(\mathbf{q}+\mathbf{H})\Omega^2 Q_{\mathbf{q}}^*\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})\\ &-\tfrac{1}{2}NQ_{\mathbf{q}}Q_{\mathbf{q}}^*\sum_{\alpha\beta} e_\alpha e_\beta \sum_{k,k'}\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha^{k'k})^*\Big[\sum_{\mathbf{H}}\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle\\ &\times\{\Omega v(\mathbf{q}+\mathbf{H})F_\beta(\mathbf{q}+\mathbf{H})-(\mathbf{q}+\mathbf{H})_\beta\Omega W'(\mathbf{q}+\mathbf{H})\}+\tfrac{1}{2}(\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}+\Delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}})I_\beta^{k'k}\Big]\Big]+\text{comp. conj.},\end{aligned} \qquad (61c)$$

$$\Delta E^{\mathrm{IV}}=\tfrac{1}{2}\sum_{ll',\alpha\beta} u_\alpha{}^l u_\beta{}^{l'}\left\{\int_{V_0(l)} d\mathbf{r}\int_{V_0(l')} d\mathbf{r}'\,\rho(\mathbf{r}'-\mathbf{r}_{l'})\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v(\mathbf{r}-\mathbf{r}')\right\}$$

$$-\{\tfrac{1}{2}i(N\Omega)^{1/2}\sum_{\mathbf{H}}\sum_{\alpha}(\mathbf{q}+\mathbf{H})_\alpha e_\alpha \rho(\mathbf{q}+\mathbf{H})v(\mathbf{q}+\mathbf{H})\Omega^2 Q_{\mathbf{q}}{}^*\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})+\text{comp. conj.}\}\,, \tag{61d}$$

$$\Delta E^{\mathrm{V}}=\tfrac{1}{2}\sum_{l\alpha\beta} u_\alpha{}^l u_\beta{}^l\left\{\int d\mathbf{r}\, n^{(0)}(\mathbf{r})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\phi_b(\mathbf{r}-\mathbf{r}_l)-\int_{V_0(l)} d\mathbf{r}\frac{\partial^2 V(\mathbf{r})}{\partial x_\alpha\partial x_\beta}\rho(\mathbf{r}-\mathbf{r}_l)\right\}. \tag{61e}$$

Substituting these results in Eq. (49) we get for the total potential energy function of the vibrating lattice:

$$\Phi^{(2)}=\tfrac{1}{2}\sum_{l\alpha\beta} u_\alpha{}^l u_\beta{}^{l'}\Phi_{\alpha\beta}{}^{ll'}+Q_{\mathbf{q}}Q_{\mathbf{q}}{}^*\sum_{\alpha\beta} e_\alpha e_\beta E_{\alpha\beta}(\mathbf{q})\,, \tag{62}$$

where for $l\neq l'$

$$\Phi_{\alpha\beta}{}^{ll'}=-\left\{\frac{\partial^2\phi^c}{\partial x_\alpha\partial x_\beta}\right\}_{\mathbf{r}=\mathbf{r}_l-\mathbf{r}_{l'}}-2\int_{V_0(l)} d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_{l'})$$
$$+\int_{V_0(l)} d\mathbf{r}\int_{V_0(l')} d\mathbf{r}'\,\rho(\mathbf{r}-\mathbf{r}_l)\rho(\mathbf{r}'-\mathbf{r}_{l'})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v(\mathbf{r}-\mathbf{r}') \tag{63}$$

and for $l=l'$

$$\Phi_{\alpha\beta}{}^{ll}=\sum_{l'\neq l}\left\{\frac{\partial^2\phi^c}{\partial x_\alpha\partial x_\beta}\right\}_{\mathbf{r}=\mathbf{r}_l-\mathbf{r}_{l'}}-2\int_{V_0(l)} d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_l)$$
$$+\int_{V_0(l)} d\mathbf{r}\int_{V_0(l)} d\mathbf{r}'\,\rho(\mathbf{r}-\mathbf{r}_l)\rho(\mathbf{r}'-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v(\mathbf{r}-\mathbf{r}')$$
$$+\int d\mathbf{r}\, n^{(0)}(\mathbf{r})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\phi_b(\mathbf{r}-\mathbf{r}_l)-\int_{V_0(l)} d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2 V(\mathbf{r})}{\partial x_\alpha\partial x_\beta}. \tag{64}$$

Using the definition of $W(\mathbf{r}-\mathbf{r}_l)$ given in Eq. (13) and the relation between $\phi_t(\mathbf{r}-\mathbf{r}_l)$ and $\phi_b(\mathbf{r}-\mathbf{r}_l)$ given in Eq. (11), we may rewrite Eq. (64) as

$$\phi_{\alpha\beta}{}^{ll}=\sum_{l'\neq l}\left\{\frac{\partial^2\phi^c}{\partial x_\alpha\partial x_\beta}\right\}_{\mathbf{r}=\mathbf{r}_l-\mathbf{r}_{l'}}-\int d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_l)+\sum_{l'\neq l}\int_{V_0(l')} d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_{l'})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}\phi_b(\mathbf{r}-\mathbf{r}_l). \tag{65}$$

$E_{\alpha\beta}$ is given by

$$E_{\alpha\beta}(\mathbf{q})=\Bigg\{-\tfrac{1}{2}N\sum_{\mathbf{H}}(\mathbf{q}+\mathbf{H})_\alpha\Omega W'(\mathbf{q}+\mathbf{H})F_\beta(\mathbf{q}+\mathbf{H})$$
$$+\tfrac{1}{2}N\sum_{k,k'}{}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^*\Big[\sum_{\mathbf{H}}\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle\{\Omega v(\mathbf{q}+\mathbf{H})F_\beta(\mathbf{q}+\mathbf{H})-(\mathbf{q}+\mathbf{H})_\beta\Omega W'(\mathbf{q}+\mathbf{H})\}$$
$$+\tfrac{1}{2}(\Delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}}+\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}})I_\beta{}^{k'k}\Big]+\text{comp. conj.}\Bigg\}. \tag{66}$$

From Eq. (62) we may immediately write down the expression for the dynamical matrix

$$D_{\alpha\beta}(\mathbf{q})=\sum_{l'}\phi_{\alpha\beta}{}^{ll'}e^{i\mathbf{q}\cdot(\mathbf{r}_{l'}-\mathbf{r}_l)}+E_{\alpha\beta}(\mathbf{q})\,, \tag{67}$$

from which the phonon frequencies may be obtained by solving the secular equation

$$|D_{\alpha\beta}-M\omega^2\delta_{\alpha\beta}|=0\,,\quad M=\text{atomic mass}. \tag{68}$$

Thus we see that we have split up the DM into two parts—one expressed in terms of force constants between pseudoatoms and a deformation contribution $E_{\alpha\beta}(\mathbf{q})$. We now discuss these contributions in some more detail. Consider the $\varphi_{\alpha\beta}{}^{ll'}(l\neq l')$ given in Eq. (63). The first term on the right represents the electrostatic interaction between the bare cores, the second term is twice the interaction between the valence charge distribution inside V_0 in the lth cell and the core plus the valence charge distributions inside V_0 in the (l')th cell (including exchange and correlation effects), while the third term subtracts off the interaction between the valence charge distributions inside the volumes V_0 in each cell. Thus the three terms together represent the force constants due to the direct interaction between the rigid pseudoatoms composed of the core plus the valence charge inside V_0. Let us split the interaction between electrons $v(\mathbf{r}-\mathbf{r}')$ into a "Hartree" part and an exchange and correlation part:

$$v(\mathbf{r}-\mathbf{r}')=v_H(\mathbf{r}-\mathbf{r}')+v_{xc}(\mathbf{r}-\mathbf{r}'). \tag{69}$$

If we take the Fourier transform of $v(\mathbf{r}-\mathbf{r}')$ to be given by Eq. (9) and choose the form (10) for $f(\mathbf{K})$, we see it is consistent to take

$$v_{xc}(\mathbf{r}-\mathbf{r}')=-\frac{1}{2}\frac{e^2}{|\mathbf{r}-\mathbf{r}'|}e^{-\xi|\mathbf{r}-\mathbf{r}'|}. \tag{70}$$

Then by our assumption of spherical symmetry for the valence charge distribution inside V_0, $\varphi_{\alpha\beta}{}^{ll'}$ as obtained from Eq. (63) splits into two parts:

$$\phi_{\alpha\beta}{}^{ll'}=(\phi_{\alpha\beta}{}^{ll'})^E+(\phi_{\alpha\beta}{}^{ll'})^R. \tag{71}$$

$(\varphi_{\alpha\beta}{}^{ll'})^E$ represents the purely electrostatic force constants as calculated between point charges $\tilde{Z}e$ where

$$\tilde{Z}=(Z-Z'), \tag{72}$$

where $+Ze$ is the core charge and $-Z'e$ is the total valence charge inside V_0. For a metal, it is obvious that one could make $(\varphi_{\alpha\beta}{}^{ll'})^E$ vanish entirely by choosing V_0 to be the whole unit cell, although we do not do so for the reasons mentioned in Sec. IV. Nevertheless for most choices of V_0, a considerable cancellation is thus explicitly obtained in what is normally taken to be the "electrostatic" contribution to the DM. The quantity $Z'e$ may be obtained from APW calculations, for instance, where it may be shown[27] that the total charge density inside the APW sphere can be expressed in terms of the logarithmic derivatives of the wave functions at the surface. The total electrostatic contribution of the $(\varphi_{\alpha\beta}{}^{ll'})^E$ may then be obtained by application of the Ewald method.[28] The remaining part of $\varphi_{\alpha\beta}{}^{ll'}$ is given by

$$(\phi_{\alpha\beta}{}^{ll'})^R=-\int_{V_0(l)}d\mathbf{r}\int_{V_0(l')}d\mathbf{r}'\times\rho(\mathbf{r}-\mathbf{r}_l)\rho(\mathbf{r}'-\mathbf{r}_{l'})\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v_{xc}(\mathbf{r}-\mathbf{r}'). \tag{73}$$

This represents a modification to the rigid pseudoatom force constants due to exchange and correlation effects. This is not to be confused with what is in general termed the "overlap" modification to the ion-ion interaction, since as mentioned in the Introduction that should really arise out of the deformation part. In fact, we may see from Eq. (70) that $v_{xc}(\mathbf{r}-\mathbf{r}')$ is an attractive interaction, due to modification of the Coulomb interaction between electrons by the exchange and correlation effects. The integral in Eq. (73) may be evaluated by standard methods[29] and gives rise to an effective short-range interaction between ions of the screened Coulomb form.

Note that we do not have to calculate the $\phi_{\alpha\beta}{}^{ll'}(l'=l)$ explicitly, since they contribute a constant to $D_{\alpha\beta}$ given by

$$\phi_{\alpha\beta}{}^{ll}=-\sum_{l'\neq l}\phi_{\alpha\beta}{}^{ll'}-\lim_{\mathbf{q}\to 0}E_{\alpha\beta}(\mathbf{q}). \tag{74}$$

We may verify this explicitly in the special case where V_0 is taken to be the whole unit cell. In this case, it may be easily verified that as $\mathbf{q}\to 0$, the $M_{k'k}$ vanish, and so does $\Delta\rho^{(1)}(\mathbf{r})$. Hence $E_{\alpha\beta}(\mathbf{q})\to 0$. Using the fact that for this choice of V_0, $W(\mathbf{r}-\mathbf{r}_l)=-\sum_{l'\neq l}\phi_t(\mathbf{r}-\mathbf{r}_l)$ for $\mathbf{r}$ inside $V_0(l)$, we obtain from Eqs. (63) and (65),

$$\sum_{l'}\phi_{\alpha\beta}{}^{ll'}=0. \tag{75}$$

Finally, we turn to the evaluation of the deformation contribution $E_{\alpha\beta}(\mathbf{q})$ from Eq. (66). We note that this contribution is expressed as a sum in wave-number space. The first term on the right of Eq. (66) is obtained directly from ΔE^{II} and represents the interaction between the external fields of the pseudoatoms and the deformation charge density. Since the latter arises self-consistently out of the residual potentials due to the pseudoatoms, we thus have an effective atom-atom coupling via the deformation charge density. It is a long-range interaction since the external potential $W'(\mathbf{r})$ of a pseudoatom goes as $-\tilde{Z}e/r$ at large distances, although as mentioned above $\tilde{Z}$ can often be made quite small by a suitable choice of V_0. The remaining terms on the right of Eq. (66) include what is conventionally termed the "overlap" interaction between neighboring atoms, and appears here as a natural consequence of our perturbation expansion. To see this we note that it arises out of second-order perturbation expressions such as

$$\sum_{k'}{}'\frac{M_{kk'}}{E_k-E_{k'}}[\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle+M_{k'k}]$$

[see for instance Eq. (44)]. $M_{kk'}$ may be regarded as the M.E. of an overlap operator in the sense that it represents the departure of the kinetic energy operator from Hermiticity in the finite volume V_0, and vanishes if the wave functions vanish on the surface of V_0, i.e., if there is no overlap. The second M.E. is none other than that of the screened potential which gives rise to the deformation charge density. Thus these terms

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[27] J. Callaway, *Energy Band Theory* (Academic Press Inc., New York, 1964), p. 99.

[28] E. W. Kellerman, Phil. Trans. Roy. Soc. London **A238**, 513 (1940).

[29] P. J. Roberts, Proc. Phys. Soc. (London) **89**, 265 (1966).

represent the overlap interaction of an atom in one unit cell with the deformation part of the wave function in that cell caused by the residual potential fields of other pseudoatoms. As before, this leads to an effective atom-atom coupling which also contains long-range components. However it is expected on physical grounds that the greater part of this interaction will be short range.

VI. SUMMARY AND DISCUSSION

We have presented a variation of the Schrödinger method for treating the electron-phonon interaction, and applied it to the problem of calculating phonon dispersion relations in solids. The first-order perturbed charge density $\Delta\rho$ is split up into a bound part $\Delta\rho^{(0)}$ and a deformation part $\Delta\rho^{(1)}$, and the ionic potential is also split up into a part which contains the deep well near the core and a residual part. The Schrödinger equation is then used to transform the matrix elements appearing in the self-consistency equation for $\Delta\rho$, to obtain an expression which gives us back the form $\Delta\rho^{(0)}+\Delta\rho^{(1)}$. What we thus obtain is a self-consistent equation for $\Delta\rho^{(1)}$ which turns out to be the response to a perturbing matrix element from which the rapidly varying part of the potential has been removed and which we call our residual potential matrix element. The physical basis for the elimination of the deep potential well near the core is clear—it has gone completely into $\Delta\rho^{(0)}$, i.e., into dragging the valence charge density near the core along with the core itself, a circumstance that remains true for all kinds of solids, whether tightly bound or not. A further transformation has then been made on the expression for the second-order perturbation of the electron energies and it has been shown how the dynamical matrix may be split up into a pseudoatom part involving force constants between rigid units composed essentially of the cores and valence charge distributions inside the volumes V_0 and a deformation part which involves the matrix elements of our residual potential, and the Fourier components of $\Delta\rho^{(1)}$.

The method depends on a reasonably accurate knowledge of the wave functions in the unperturbed crystal, such as may be obtained from an accurate band-structure calculation. We have emphasized the application of the APW formalism to our method because the APW method has proved to be both accurate and versatile in performing band-structure calculations for a wide variety of solids,[19] and APW wave functions have been used already to calculate quantities like x-ray form factors[30] and positron annihilation in solids.[31] In addition, as discussed in Sec. III, the nature of the APW scheme seems to make it particularly suitable to apply to our transformation scheme.

Since we intend to apply the formalism eventually to the transition metals, we have not been able to simplify the matrix elements of the form $\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle$ that appear in our formalism, and this has unavoidably led to an increase in complexity for the expressions obtained. These would simplify considerably if we applied our method also to the case of the free-electron metals. We believe that in this case, the method might have some advantages over the pseudopotential methods. By explicitly separating out a part of what is conventionally calculated as the band-structure contribution and lumping it together with the pseudoatom contribution to the dynamical matrix, we have achieved to some extent the explicit cancellation between the conventional electrostatic and band-structure contribution. Since our matrix elements and dielectric function, etc., are only involved in the residual deformation part, we believe that errors in calculating the latter will not be quite so critical as in the conventional pseudopotential formalism. Further, the energies of the core states, and the details of the ionic potential near the cores (involving exchange and correlation with the core electrons) are not explicitly involved. We may also note that the discontinuity in the Heine-Abarenkov potential which causes oscillations in its Fourier transform and convergence difficulties for the band-structure part is not present in the matrix elements of our residual potential, as discussed in Sec. V. In conclusion, we might say that at the expense of not being able to apply the method to such a variety of properties as the pseudopotential method, the present formalism offers a potentially more accurate method for lattice dynamics calculations, and is applicable to a wide range of solids.

The main practical difficulties we anticipate in actual application are (1) sensitivities of the wave functions from band-structure calculations to the crystal potentials used, which are in any case rarely self-consistent, and (2) possible poor convergence in the sums over excited states k' in calculating $E_{\alpha\beta}(\mathbf{q})$ from Eq. (66). We believe that the first problem may not be too serious provided we are consistent in calculating $W(\mathbf{r}-\mathbf{r}_l)$ from Eq. (13) in terms of the *same* atomic potentials used to build up the crystal potential utilized in the band-structure calculation. One also hopes that, as discussed in Sec. II, removal of the $\Delta\rho^{(0)}$ part helps improve the convergence of the sum over k'. Needless to say these points may only be checked by an actual calculation. It should be noted, however, that as discussed previously, the last two terms in $E_{\alpha\beta}$ as calculated from Eq. (66) contain a large portion of what is effectively the overlap interaction between neighboring atoms, which is known from experiment to drop off rapidly with increasing neighbor distance. Thus it is possible that the sum in wave-vector space may not be rapidly convergent, and special methods may have to be used to improve the convergence of the sum. Details will be published in a forthcoming paper.

After the inception of this work, a recent paper by Golibersuch[32] on the electron-phonon interaction by

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[30] F. J. Arlinghaus, Phys. Rev. (to be published).

[31] T. L. Loucks, Phys. Rev. 144, 504 (1966).

[32] D. C. Golibersuch, Phys. Rev. 157, 532 (1967).

the APW method was brought to the author's attention. Golibersuch obtains a formula for the EPME by assuming that the lattice perturbation corresponds essentially to a rigid displacement of the muffin tins centered on the ion cores, and further he considers only the case of energy-conserving transitions. No attempt is made to consider the effect of the electron response in a self-consistent manner. A comparison of his formula for the total EPME with ours for the particular case of energy-conserving transitions shows that his assumption is equivalent to keeping only the term $I_\alpha^{k'k}$ in Eq. (44). Further, the absence of the $(E_k - E_{k'})$ term in his EPME implies that one cannot use it as it stands for a calculation of the phonon frequencies.

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APPENDIX A

Inside the APW sphere of radius r_s centered on the lattice site r_ν, the APW wave function may be written as[19]

$$\psi_k(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} 4\pi e^{i\mathbf{k}\cdot\mathbf{r}_\nu} \sum_{\mathbf{H}} a_{\mathbf{H}}^k \sum_{l=0}^{\infty} \sum_{m=-l}^{+l} i^l j_l(|\mathbf{k}+\mathbf{H}| r_s) \times \frac{u_l(\rho)}{u_l(r_s)} Y_{lm}^*(\mathbf{k}+\mathbf{H}) Y_{lm}(\theta,\varphi)\,, \quad \text{(A1)}$$

where the mixing coefficients $a_{\mathbf{H}}$ of the APW's are normalized such that $\psi_k^* \psi_k$ is normalized to unity in the volume Ω; the coordinates of $\mathbf{r}$ relative to $\mathbf{r}_\nu$ are expressed in terms of (ρ,θ,φ) in spherical coordinates, and $u_l(r)$ is the radial solution to the Schrödinger equation inside $V_0(\nu)$ with angular momentum l.

Substituting these wave functions into Eq. (33b), and using Eq. (6), we get

$$M_{k'k} = i(N/\Omega)^{1/2} [Q_q \Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}} + Q_q^* \Delta_{\mathbf{k}'-\mathbf{k},-\mathbf{q}}] J_{k'k}\,, \quad \text{(A2)}$$

where $\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}$ is unity if $\mathbf{k}' = \mathbf{k}+\mathbf{q}$ modulus a reciprocal lattice vector, and zero otherwise. (We are working in the reduced zone scheme such that the state k is specified by a wave vector $\mathbf{k}$ in the first zone and a band index which we shall not need to write explicitly.)

$$J_{k'k} = \frac{\hbar^2}{2m} 16\pi^2 r_s^2 \sum_{\mathbf{H},\mathbf{H}} (a_{\mathbf{H}'}^{k'})^* a_{\mathbf{H}}^k \sum_{l,l'=0}^{\infty} \sum_{m,m'} i^{(l+l'-1)} (-1)^{l'} \frac{j_{l'}(|\mathbf{k}'+\mathbf{H}'| r_s)}{u_{l'}^*(r_s)} \frac{j_l(|\mathbf{k}+\mathbf{H}| r_s)}{u_l(r_s)} Y_{l'm'}(\mathbf{k}'+\mathbf{H}') Y_{lm}^*(\mathbf{k}+\mathbf{H})$$
$$\times \left\{ \sum_\alpha e_\alpha \int_{S_0} d\Omega \left[u_{l'}'^*(r_s) Y_{l'm'}^*(\theta,\varphi) \frac{\partial}{\partial x_\alpha} [u_l(\rho) Y_{lm}(\theta,\varphi)]_{\rho=r_s} \right.\right.$$
$$\left.\left. - u_{l'}^*(r_s) Y_{l'm'}^*(\theta,\varphi) \frac{\partial}{\partial x_\alpha} [u_l'(\rho) Y_{lm}(\theta,\varphi)]_{\rho=r_s} \right] \right\}\,, \quad \text{(A3)}$$

where $u'(r)$ denotes a radial derivative. Let us transform to a spherical basis for the e_α, thus

$$\begin{bmatrix} \xi_1 \\ \xi_0 \\ \xi_{-1} \end{bmatrix} = \begin{bmatrix} -1/\sqrt{2} & -i/\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 1/\sqrt{2} & -i/\sqrt{2} & 0 \end{bmatrix} \begin{bmatrix} e_1 \\ e_2 \\ e_3 \end{bmatrix}. \quad \text{(A4)}$$

Then, using the gradient operator theorem,[33] we have the result that

$$\sum_\alpha e_\alpha \int d\Omega\, Y_{l'm'}^*(\theta,\varphi) \frac{\partial}{\partial x_\alpha} \{\phi(r) Y_{lm}(\theta,\varphi)\}_{r=r_s} = -\left(\frac{l+1}{2l+1}\right)^{1/2} \left(\phi'(r_s) - \frac{l}{r_s}\phi(r_s)\right) C_{m',m-m'}{}^{l+1,1,l} \delta_{l',l+1} \xi_{m-m'}$$
$$+ \left(\frac{l}{2l+1}\right)^{1/2} \left(\phi'(r_s) + \frac{l+1}{r_s}\phi(r_s)\right) C_{m',m-m'}{}^{l-1,1,l} \delta_{l',l-1} \xi_{m-m'}\,,$$

where $\phi(r)$ is any radial function and the C's are the Clebsh-Gordan coefficients. Substituting this result back in Eq. (A3), and using the radial Schrödinger equation for the $u_l(r)$, we obtain finally

$$M_{k'k} = i(N/\Omega)^{1/2} [Q_{\mathbf{q}} \Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}} + Q_{\mathbf{q}}^* \Delta_{\mathbf{k}'-\mathbf{k},-\mathbf{q}}] \sum_\alpha e_\alpha I_\alpha^{k'k}\,, \quad \text{(A5)}$$

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[33] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957), p. 124.

where

$$I_\alpha{}^{k'k}=\frac{\hbar^2}{2m}16\pi^2r_s{}^2\sum_{\mathbf{H},\mathbf{H}}(a_{\mathbf{H}'}{}^{k'})^*a_{\mathbf{H}}{}^k\sum_{lm}j_l(|k+\mathbf{H}|r_s)Y_{lm}{}^*(\mathbf{k}+\mathbf{H})$$

$$\times\sum_{m'=m-1}^{m+1}\bigg[j_{l+1}(|\mathbf{k}'+\mathbf{H}'|r_s)Y_{l+1,m'}(\mathbf{k}'+\mathbf{H}')C_{m',m-m'}{}^{l+1,1,l}\left(\frac{l+1}{2l+1}\right)^{1/2}$$

$$\times\left\{\frac{l(l+1)}{r_s{}^2}+\frac{2m}{\hbar^2}[V(r_s)-E_k]-\left(\frac{2}{r_s}+\frac{u_{l+1}{}'(r_s)}{u_{l+1}(r_s)}\right)\frac{u_l{}'(r_s)}{u_l(r_s)}+\frac{l}{r_s}\left(\frac{u_{l+1}{}'(r_s)}{u_{l+1}(r_s)}-\frac{u_l{}'(r_s)}{u_l(r_s)}\right)\right\}$$

$$+j_{l-1}(|\mathbf{k}'+\mathbf{H}'|r_s)Y_{l-1,m'}(\mathbf{k}'+\mathbf{H}')C_{m',m-m'}{}^{l-1,1,l}\left(\frac{l}{2l+1}\right)^{1/2}$$

$$\times\left\{\frac{l(l+1)}{r_s{}^2}+\frac{2m}{\hbar^2}[V(r_s)-E_k]-\left(\frac{2}{r_s}+\frac{u_{l-1}{}'(r_s)}{u_{l-1}(r_s)}\right)\frac{u_l{}'(r_s)}{u_l(r_s)}+\frac{(l+1)}{r_s}\left(\frac{u_l{}'(r_s)}{u_l(r_s)}-\frac{u_{l-1}{}'(r_s)}{u_{l-1}(r_s)}\right)\right\}\bigg]A_{m-m',\alpha}, \qquad (A6)$$

where $A_{i\alpha}$ is the matrix defined in Eq. (A4).

The logarithmic derivatives (u_l'/u_l) are calculated in the APW calculation, along with the coefficients $a_{\mathbf{H}}{}^k$ and the energy E_k. The $u_l(r_s)$ are to be evaluated at energy E_k and the $u_{l\pm1}(r_s)$ at energy $E_{k'}$.

APPENDIX B

If $n(k)$ denotes the occupation number of state k, the first-order perturbed electron density is given by

$$\Delta\rho=\sum_k n(k)\{\psi_k{}^*\Delta\psi_k+\psi_k\Delta\psi_k{}^*\}. \qquad (B1)$$

Substituting in this the result in Eq. (35) we obtain

$$\Delta\rho(\mathbf{r})=-\sum_{l,\alpha}u_\alpha{}^l\gamma(\mathbf{r}-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}n^{(0)}(\mathbf{r})$$
$$+\sum_{k,k'}{}'\frac{n(k)}{E_k-E_{k'}}\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}$$
$$+\Delta V^{\mathrm{II}}|\psi_k\rangle+M_{k'k}\}\psi_{k'}(\mathbf{r})\psi_k{}^*(\mathbf{r})$$
$$+\sum_{k,k'}{}'\frac{n(k)}{E_k-E_{k'}}\{\langle\psi_k|\Delta V^{\mathrm{I}}$$
$$+\Delta V^{\mathrm{II}}|\psi_{k'}\rangle+M_{k'k}{}^*\}\psi_{k'}{}^*(\mathbf{r})\psi_k(\mathbf{r}), \qquad (B2)$$

where $n^{(0)}(\mathbf{r})$ is the unperturbed valence charge density. Now by using Schrödinger's equation we may derive the following important relation between $M_{k'k}$ and its Hermitian conjugate:

$$M_{k'k}{}^*=M_{kk'}+\sum_{l,\alpha}u_\alpha{}^l(E_k-E_{k'})\int_{S_0(l)}dS_\alpha\psi_k{}^*\psi_{k'}, \qquad (B3)$$

where dS_α denotes the α component of the vector $\mathbf{dS}$. Thus, by interchanging k and k' in the sum in the last term of Eq. (B2) we obtain

$$\Delta\rho(\mathbf{r})=-\sum_{l,\alpha}u_\alpha{}^l\bigg\{\gamma(\mathbf{r}-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}n^{(0)}(\mathbf{r})$$
$$-\sum_{k,k'}{}'n(k)\psi_{k'}{}^*(\mathbf{r})\psi_k(\mathbf{r})\int_{S_0(l)}dS_\alpha{}'$$
$$\times\psi_k{}^*(\mathbf{r}')\psi_{k'}(\mathbf{r}')\bigg\}+\sum_{k,k'}{}'\frac{n(k)-n(k')}{E_k-E_{k'}}$$
$$\times\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle+M_{k'k}\}. \qquad (B4)$$

We shall now prove that the first term in curly brackets in (B4) is $\partial\rho(\mathbf{r}-\mathbf{r}_l)/\partial x_\alpha$ as defined in Eq. (8). The Fourier transform of $\partial\rho(\mathbf{r}-\mathbf{r}_l)/\partial x_\alpha$ is

$$iK_\alpha\rho(\mathbf{K})e^{-i\mathbf{K}\cdot\mathbf{r}_l},$$

where

$$\rho(\mathbf{K})=\frac{1}{\Omega}\int_{V_0(l)}d\mathbf{r}\,n^{(0)}(\mathbf{r})e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)}. \qquad (B5)$$

The transform of the first expression in curly brackets in (B4) is

$$e^{-i\mathbf{K}\cdot\mathbf{r}_l}\frac{1}{\Omega}\int_{V_0(l)}d\mathbf{r}\left\{\frac{\partial}{\partial x_\alpha}n^{(0)}(\mathbf{r})\right\}e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)}$$
$$-\sum_{k,k'}{}'\frac{1}{\Omega}n(k)\int_{S_0(l)}dS_\alpha\,\psi_k{}^*\psi_{k'}\langle\psi_{k'}|e^{-i\mathbf{K}\cdot\mathbf{r}}|\psi_k\rangle. \qquad (B6)$$

Since by the Bloch theorem the second term vanishes for $k=k'$ and finite $\mathbf{q}$, we may formally include this term in the sum. Then applying the completeness property of the $\psi_{k'}$ to the second term of (B6), we may write the equation as

$$e^{-i\mathbf{K}\cdot\mathbf{r}_l}\frac{1}{\Omega}\left[\int_{V_0(l)} d\mathbf{r}\left\{\frac{\partial}{\partial x_\alpha}n^{(0)}(\mathbf{r})\right\}e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)} - \int_{S_0(l)} dS_\alpha\, n^{(0)}(\mathbf{r})e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)}\right],$$

which by the divergence theorem may be rewritten as

$$-e^{-i\mathbf{K}\cdot\mathbf{r}_l}\frac{1}{\Omega}\left[\int_{V_0(l)} d\mathbf{r}\, n^{(0)}(\mathbf{r})\frac{\partial}{\partial x_\alpha}\{e^{-i\mathbf{K}\cdot(\mathbf{r}-\mathbf{r}_l)}\}\right] = iK_\alpha\rho(\mathbf{K})e^{-i\mathbf{K}\cdot\mathbf{r}_l}. \quad \text{(B7)}$$

Hence we see that the first term on the right of Eq. (B4) is exactly $\Delta\rho^{(0)}(\mathbf{r})$ as defined in Eq. (8), and hence the second term must be identified with the deformation part $\Delta\rho^{(1)}$.

APPENDIX C

Consider the equation

$$\Delta\rho = \Delta\rho^{(0)} + \Delta\rho^{(1)}. \quad \text{(C1)}$$

Let us now choose slightly different definitions of $\Delta\rho^{(0)}$ and $\Delta\rho^{(1)}$. Specifically we define a new $\Delta\tilde{\rho}^{(0)}$ which is equal to the first term on the right of Eq. (B2), and a new $\Delta\tilde{\rho}^{(1)}$ equal to the rest of the perturbation.

Then using Eq. (B2) and remembering the old definitions of ΔV^{I} [Eq. (20)] and ΔV^{II} [Eq. (22)], we get a new self-consistency equation for $\Delta\tilde{\rho}^{(1)}$:

$$\Delta\tilde{\rho}^{(1)} = \sum_{k,k'}{}' \frac{n(k)}{E_k - E_{k'}}\{\langle\psi_{k'}|\Delta\tilde{V}^{\mathrm{I}} + \Delta\tilde{V}^{\mathrm{II}}|\psi_k\rangle + M_{k'k}\} \times \psi_{k'}\psi_k^* + \text{comp. conj.}, \quad \text{(C2)}$$

where

$$\Delta\tilde{V}^{\mathrm{II}}(\mathbf{r}) = \int d\mathbf{r}'\,\Delta\tilde{\rho}^{(1)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}') \quad \text{(C3)}$$

and

$$\Delta\tilde{V}^{\mathrm{I}}(\mathbf{r}) = -\sum_{l,\alpha} u_\alpha{}^l \frac{\partial}{\partial x_\alpha}W(\mathbf{r}-\mathbf{r}_l) + \int d\mathbf{r}'\,\{\Delta\tilde{\rho}^{(0)}(\mathbf{r}') - \Delta\rho^{(0)}(\mathbf{r}')\}v(\mathbf{r}-\mathbf{r}'). \quad \text{(C4)}$$

Now

$$\int d\mathbf{r}'\,\Delta\tilde{\rho}^{(0)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}') = -\sum_{l,\alpha} u_\alpha{}^l \int_{V_0(l)} d\mathbf{r}' \frac{\partial}{\partial x_\alpha{}'}n^{(0)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}') \quad \text{(C5)}$$

and

$$\begin{aligned}\int d\mathbf{r}'\,\Delta\rho^{(0)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}') &= -\sum_{l,\alpha} u_\alpha{}^l \int d\mathbf{r}' \frac{\partial}{\partial x_\alpha{}'}\{n^{(0)}(\mathbf{r}')\gamma(\mathbf{r}'-\mathbf{r}_l)\}v(\mathbf{r}-\mathbf{r}') \\ &= \sum_{l,\alpha} u_\alpha{}^l \int d\mathbf{r}'\, n^{(0)}(\mathbf{r}')\gamma(\mathbf{r}'-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha{}'}v(\mathbf{r}-\mathbf{r}') \\ &= \sum_{l,\alpha} u_\alpha{}^l \int_{V_0(l)} d\mathbf{r}'\, n^{(0)}(\mathbf{r}')\frac{\partial}{\partial x_\alpha{}'}v(\mathbf{r}-\mathbf{r}') \qquad \text{(C6)}\end{aligned}$$

$$\begin{aligned}\therefore \int d\mathbf{r}'\,\{\Delta\tilde{\rho}^{(0)}(\mathbf{r}') - \Delta\rho^{(0)}(\mathbf{r}')\} &= -\sum_{l,\alpha} u_\alpha{}^l \int_{S_0(l)} dS_\alpha{}'\, n^{(0)}(\mathbf{r}')v(\mathbf{r}-\mathbf{r}') \\ &= -\sum_{l,\alpha} u_\alpha{}^l\rho(r_s) \int_{V_0(l)} d\mathbf{r}' \frac{\partial}{\partial x_\alpha{}'}v(\mathbf{r}-\mathbf{r}') \\ &= \sum_{l,\alpha} u_\alpha{}^l \int_{V_0(l)} d\mathbf{r}'\,\rho(r_s)\frac{\partial}{\partial x_\alpha}v(\mathbf{r}-\mathbf{r}'), \qquad \text{(C7)}\end{aligned}$$

where $\rho(r_s)$ is the value of the unperturbed valence charge density at the surface of $V_0(l)$ and is assumed to be spherically symmetric. In deriving Eq. (C7) we have used the divergence theorem and the fact that

$$\frac{\partial}{\partial x_\alpha{}'}v(\mathbf{r}-\mathbf{r}') = -\frac{\partial}{\partial x_\alpha}v(\mathbf{r}-\mathbf{r}'). \quad \text{(C8)}$$

Hence Eq. (C4) becomes

$$\Delta\tilde{V}^{\mathrm{I}}(\mathbf{r}) = -\sum_{l,\alpha} u_\alpha{}^l \frac{\partial}{\partial x_\alpha}W''(\mathbf{r}-\mathbf{r}_l), \quad \text{(C9)}$$

where

$$W''(\mathbf{r}-\mathbf{r}_l) = W(\mathbf{r}-\mathbf{r}_l) - \int_{V_0(l)} d\mathbf{r}'\,\rho(r_s)v(\mathbf{r}-\mathbf{r}'). \quad \text{(C10)}$$

As discussed in the text, $W''(\mathbf{r}-\mathbf{r}_l)$ equals $-Z^*/r$ for $r > r_s$ where Z^* is the effective valence on the core.

APPENDIX D

From Eq. (B4) we see that by making use of the completeness property of the $\psi_{k'}$ we may write $\Delta\rho^{(0)}(\mathbf{r})$ as

$$\Delta\rho^{(0)}(\mathbf{r}) = -\sum_{l,\alpha} u_\alpha{}^l \left\{\gamma(\mathbf{r}-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}n^{(0)}(\mathbf{r}) - \int_{S_0(l)} dS_\alpha{}'\,\delta(\mathbf{r}-\mathbf{r}')n^{(0)}(\mathbf{r}')\right\}. \quad \text{(D1)}$$

Using this result and the expression for ΔV^{I} given in Eq. (19), we get

$$\Delta E^{\mathrm{I}}=\tfrac{1}{2}\sum_{ll',\alpha\beta}(\phi_{\alpha\beta}{}^{ll'})^{\mathrm{I}}u_\alpha{}^l u_\beta{}^{l'}, \tag{D2}$$

where

$$\begin{aligned}(\phi_{\alpha\beta}{}^{ll'})^{\mathrm{I}}&=\int_{V_0(l)}d\mathbf{r}\frac{\partial}{\partial x_\alpha}W(\mathbf{r}-\mathbf{r}_l{}')\frac{\partial}{\partial x_\beta}n^{(0)}(\mathbf{r})\\&\quad-\int_{S_0(l)}dS_\beta\left\{\frac{\partial}{\partial x_\alpha}W(\mathbf{r}-\mathbf{r}_{l'})\right\}n^{(0)}(\mathbf{r})\\&=-\int_{V_0(l)}d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_{l'}),\end{aligned} \tag{D3}$$

where we have used the fact that inside $V_0(l)$, $n^{(0)}(\mathbf{r})=\rho(\mathbf{r}-\mathbf{r}_l)$. We shall find it more convenient to express ΔE^{II} as a reciprocal lattice sum. For this purpose we make use of a well-known theorem in Fourier analysis:

$$\int d\mathbf{r}\,F(\mathbf{r})G(\mathbf{r})=\Omega\sum_{\mathbf{K}}F(\mathbf{K})G^*(\mathbf{K}). \tag{D4}$$

We shall also frequently make use of the fact that since all our potentials and charge densities are real, $G^*(\mathbf{K})=G(-\mathbf{K})$. Further, since our potentials are even functions of $\mathbf{r}$ we shall take $W''(\mathbf{K})=W''(-\mathbf{K})$, etc. Making use of Eq. (29) we get

$$\begin{aligned}\Delta E^{\mathrm{II}}=-\tfrac{1}{2}i(N\Omega)^{1/2}\sum_{\mathbf{H}}\sum_{\alpha}(\mathbf{q}+\mathbf{H})_\alpha e_\alpha W'(\mathbf{q}+\mathbf{H})\Omega\\\times Q_{\mathbf{q}}[\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})]^*+\text{comp. conj.}\end{aligned} \tag{D5}$$

Using the representation for $\Delta\rho^{(1)}$ given in Eq. (42), we get the expression for ΔE^{II} in Eq. (61b). To obtain ΔE^{III}, we first use Eq. (37) for $\Delta\rho^{(1)}(\mathbf{r})$ to transform back into the form

$$\begin{aligned}\Delta E^{\mathrm{III}}=\tfrac{1}{2}\sum_{k,k'}{}'\frac{n(k)}{E_k-E_{k'}}\\\times\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle\langle\psi_k|\Delta V^{\mathrm{III}}|\psi_{k'}\rangle\\+\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle\langle\psi_k|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_{k'}\rangle\\+M_{k'k}\langle\psi_k|\Delta V^{\mathrm{III}}|\psi_{k'}\rangle+M_{kk'}\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle\}.\end{aligned} \tag{D6}$$

Using the identity (32) for $\langle\psi_{k'}|\Delta V^{\mathrm{III}}|\psi_k\rangle$ we obtain

$$\Delta E^{\mathrm{III}}=\Delta E_a{}^{\mathrm{III}}+\Delta E_b{}^{\mathrm{III}}+\Delta E_c{}^{\mathrm{III}}+\Delta E_d{}^{\mathrm{III}}, \tag{D7}$$

where

$$\begin{aligned}\Delta E_a{}^{\mathrm{III}}=\tfrac{1}{2}\sum_{l,\alpha}u_\alpha{}^l\sum_{k,k'}n(k)\bigg\{\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle\\\times\int_{V_0(l)}d\mathbf{r}\,\psi_k{}^*\frac{\partial}{\partial x_\alpha}\psi_{k'}-\langle\psi_k|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_{k'}\rangle\\\times\int_{V_0(l)}d\mathbf{r}\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k\bigg\},\end{aligned} \tag{D8a}$$

$$\begin{aligned}\Delta E_b{}^{\mathrm{III}}=\tfrac{1}{2}\sum_{k,k'}{}'\frac{n(k)-n(k')}{E_k-E_{k'}}\\\times\langle\psi_{k'}|\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}|\psi_k\rangle M_{kk'},\end{aligned} \tag{D8b}$$

$$\begin{aligned}\Delta E_c{}^{\mathrm{III}}=\tfrac{1}{2}\sum_{l,\alpha}u_\alpha{}^l\sum_{k,k'}n(k)\bigg\{M_{k'k}\int_{V_0(l)}d\mathbf{r}\,\psi_k{}^*\frac{\partial}{\partial x_\alpha}\psi_{k'}\\-M_{kk'}\int_{V_0(l)}d\mathbf{r}\,\psi_{k'}{}^*\frac{\partial}{\partial x_\alpha}\psi_k\bigg\},\end{aligned} \tag{D8c}$$

$$\Delta E_d{}^{\mathrm{III}}=\tfrac{1}{2}\sum_{k,k'}{}'\frac{n(k)-n(k')}{E_k-E_{k'}}M_{k'k}M_{kk'}. \tag{D8d}$$

Note that again we have formally included the terms $k'=k$ in $\Delta E_a{}^{\mathrm{III}}$ and $\Delta E_c{}^{\mathrm{III}}$ since such terms vanish for $\mathbf{q}\neq 0$. We may then use the completeness property of the $\psi_{k'}$ to obtain

$$\begin{aligned}\Delta E_a{}^{\mathrm{III}}&=\tfrac{1}{2}\sum_{l,\alpha}u_\alpha{}^l\sum_k n(k)\int_{V_0(l)}d\mathbf{r}\\&\quad\times\bigg\{\psi_k{}^*\frac{\partial}{\partial x_\alpha}[(\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}})\psi_k]\\&\qquad-\psi_k{}^*(\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}})\frac{\partial}{\partial x_\alpha}\psi_k\bigg\}\\&=\tfrac{1}{2}\sum_{l,\alpha}u_\alpha{}^l\int_{V_0(l)}d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}(\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}})\\&=\tfrac{1}{2}\sum_{ll',\alpha\beta}(\phi_{\alpha\beta}{}^{ll'})^{\mathrm{III}}u_\alpha{}^l u_\beta{}^{l'}\\&\quad+\tfrac{1}{2}\sum_{l,\alpha}u_\alpha{}^l\int_{V_0(l)}d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial}{\partial x_\alpha}\Delta V^{\mathrm{II}}(\mathbf{r}),\end{aligned} \tag{D9}$$

where

$$(\phi_{\alpha\beta}{}^{ll'})^{\mathrm{III}}=-\int_{V_0(l)}d\mathbf{r}\,\rho(\mathbf{r}-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}W(\mathbf{r}-\mathbf{r}_{l'}). \tag{D10}$$

Applying Eqs. (30) and (D4) to the second term of Eq. (D9) we get finally

$$\begin{aligned}\Delta E_a{}^{\mathrm{III}}=\tfrac{1}{2}\sum_{ll',\alpha\beta}(\phi_{\alpha\beta}{}^{ll'})^{\mathrm{III}}u_\alpha{}^l u_\beta{}^{l'}\\+\{\tfrac{1}{2}i(N\Omega)^{1/2}\sum_{\mathbf{H}}\sum_{\alpha}(\mathbf{q}+\mathbf{H})_\alpha e_\alpha\rho(\mathbf{q}+\mathbf{H})v(\mathbf{q}+\mathbf{H})\Omega^2\\\times Q_{\mathbf{q}}[\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})]+\text{comp. conj.}\}.\end{aligned} \tag{D11}$$

To evaluate $\Delta E_b^{\mathrm{III}}$ let us write

$$\Delta V^{\mathrm{I}}+\Delta V^{\mathrm{II}}=\sum_{\mathbf{H}}\{V(\mathbf{q}+\mathbf{H})e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}+V^*(\mathbf{q}+\mathbf{H})e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}\},\quad\text{(D12)}$$

since we know that these are the only nonvanishing Fourier components of the perturbing potential. Then we may write

$$\Delta E_b^{\mathrm{III}}=\tfrac{1}{2}{\sum_{k,k'}}'\frac{n(k)-n(k')}{E_k-E_{k'}}\times\sum_{\mathbf{H}}\{V(\mathbf{q}+\mathbf{H})\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle M_{kk'}+V^*(\mathbf{q}+\mathbf{H})\langle\psi_k|e^{-i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle M_{k'k}\},\quad\text{(D13)}$$

where we have interchanged k,k' in the summation in the second term. Using Eq. (B3) to transform the first term, we may write this as

$$\Delta E_b^{\mathrm{III}}=\left\{\tfrac{1}{2}{\sum_{k,k'}}'\frac{n(k)-n(k')}{E_k-E_{k'}}V(\mathbf{q}+\mathbf{H})\times\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle M_{k'k}^*+\text{comp. conj.}\right\}-\tfrac{1}{2}\sum_{k,k'}\{n(k)-n(k')\}\sum_{\mathbf{H}}V(\mathbf{q}+\mathbf{H})\times\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle\sum_{l,\alpha}u_\alpha{}^l\int_{S_0(l)}dS_\alpha\,\psi_{k'}\psi_k^*.\quad\text{(D14)}$$

By using the expression for $V(\mathbf{q}+\mathbf{H})$ obtained from Eqs. (29) and (30), and for $M_{kk'}$ given in Eq. (A5) we may show that the first term yields

$$\Delta E_b^{\mathrm{III}}=\tfrac{1}{2}NQ_{\mathbf{q}}Q_{\mathbf{q}}^*\sum_{\alpha\beta}e_\alpha e_\beta\sum_{\mathbf{H}}{\sum_{k,k'}}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}\times(I_\alpha{}^{k'k})^*\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle\times[\Omega v(\mathbf{q}+\mathbf{H})F_\beta(\mathbf{q}+\mathbf{H})-(\mathbf{q}+\mathbf{H})_\beta\Omega W'(\mathbf{q}+\mathbf{H})]+\text{comp. conj.}\quad\text{(D15)}$$

The second term vanishes since it may be written as

$$-{\sum_{l,\alpha}}'\tfrac{1}{2}u_\alpha{}^l\sum_{\mathbf{H}}V(\mathbf{q}+\mathbf{H})\left\{{\sum_{k,k'}}'n(k)\langle\psi_{k'}|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_k\rangle\times\int dS_\alpha\psi_{k'}\psi_k^*-{\sum_{k,k'}}'n(k)\langle\psi_k|e^{i(\mathbf{q}+\mathbf{H})\cdot\mathbf{r}}|\psi_{k'}\rangle\times\int_{S_0(l)}dS_\alpha\psi_k\psi_{k'}^*\right\}.\quad\text{(D16)}$$

In the second term we have interchanged the indices k,k' appearing in the sum. Formally including the term $k=k'$ and using the completeness property of the $\psi_{k'}$ we may show that the two terms in the curly brackets cancel.

To evaluate $\Delta E_d^{\mathrm{III}}$ we use Eq. (B3) to transform $M_{kk'}$ and obtain

$$\Delta E_d^{\mathrm{III}}=\tfrac{1}{2}{\sum_{k,k'}}'\frac{n(k)-n(k')}{E_k-E_{k'}}M_{k'k}M_{k'k}^*-\tfrac{1}{2}{\sum_{k,k'}}'\{n(k)-n(k')\}M_{k'k}\times\sum_{l,\alpha}u_\alpha{}^l\int_{V_0(l)}d\mathbf{r}\frac{\partial}{\partial x_\alpha}(\psi_k^*\psi_{k'}).\quad\text{(D17)}$$

Using Eq. (A5), the first term may be written as

$$(E_d^{\mathrm{III}})_1=\tfrac{1}{2}NQ_{\mathbf{q}}Q_{\mathbf{q}}^*\sum_{\alpha\beta}e_\alpha e_\beta\times{\sum_{k,k'}}'\frac{1}{\Omega}\frac{n(k)-n(k')}{E_k-E_{k'}}(I_\alpha{}^{k'k})^*I_\beta{}^{k'k}\times\tfrac{1}{2}(\Delta_{\mathbf{k}'-\mathbf{k},\mathbf{q}}+\Delta_{\mathbf{k}-\mathbf{k}',\mathbf{q}})+\text{comp. conj.}\quad\text{(D18)}$$

Interchanging one of the sums over k,k' in the second term we may write it as

$$(\Delta E_d^{\mathrm{III}})_2=-\tfrac{1}{2}\sum_{l,\alpha}u_\alpha{}^l{\sum_{k,k'}}'n(k)\times\left[M_{k'k}\int_{V_0(l)}d\mathbf{r}\frac{\partial}{\partial x_\alpha}(\psi_k^*\psi_{k'})-M_{kk'}\int_{V_0(l)}d\mathbf{r}\frac{\partial}{\partial x_\alpha}(\psi_{k'}^*\psi_k)\right].\quad\text{(D19)}$$

In Appendix E, we combine this term with $\Delta E_C^{\mathrm{III}}$ to show that their sum vanishes identically or else contributes a constant term to the dynamical matrix which may be absorbed in $\Phi_{\alpha\beta}{}^{ll}$. Using Eq. (D1) and Eq. (57) for ΔV^{IV} we may show exactly as for the result in Eq. (D3) that the first term of ΔE^{IV} may be written as

$$\tfrac{1}{2}\sum_{ll',\alpha\beta}(\Phi_{\alpha\beta}{}^{ll'})^{\mathrm{IV}}u_\alpha{}^lu_\beta{}^{l'},$$

where

$$(\Phi_{\alpha\beta}{}^{ll'})^{\mathrm{IV}}=\int_{V_0(l)}d\mathbf{r}\int_{V_0(l)}d\mathbf{r}'\times\rho(\mathbf{r}'-\mathbf{r}_l)\frac{\partial^2}{\partial x_\alpha\partial x_\beta}v(\mathbf{r}-\mathbf{r}').\quad\text{(D20)}$$

By using arguments similar to those used in deriving Eq. (D5) we get for the second term the expression

$$-\{\tfrac{1}{2}i(N\Omega)^{1/2}\sum_{\mathbf{H}}\sum_{\alpha}(\mathbf{q}+\mathbf{H})_{\alpha}e_{\alpha}\rho(\mathbf{q}+\mathbf{H})v(\mathbf{q}+\mathbf{H})\Omega^{2} \times Q_{\mathbf{q}}{}^{*}\Delta\rho^{(1)}(\mathbf{q}+\mathbf{H})+\text{comp. conj.}\}.$$

Thus ΔE^{IV} is given by Eq. (61d) in the text. Again using Eq. (D1) and the expression for ΔE^{III} given in Eq. (21) we may use arguments similar to those used in deriving Eqs. (D3) and (D20) to show that

$$\frac{1}{2}\int d\mathbf{r}\,\Delta V^{\mathrm{III}}(\mathbf{r})\Delta\rho^{(0)}(\mathbf{r}) = -\tfrac{1}{2}\sum_{l\alpha\beta}u_{\alpha}{}^{l}u_{\beta}{}^{l}\int_{V_0(l)}d\mathbf{r}\frac{\partial^2 V(r)}{\partial x_{\alpha}\partial x_{\beta}}\rho(\mathbf{r}-\mathbf{r}_l).$$

Finally, using Eq. (53) for $\Delta V_b{}^{(2)}$ we obtain

$$\int d\mathbf{r}\,n^{(0)}(\mathbf{r})\Delta V_b{}^{(2)}(\mathbf{r}) = \tfrac{1}{2}\sum_{l\alpha\beta}u_{\alpha}{}^{l}u_{\beta}{}^{l}\int d\mathbf{r}\,n^{(0)}(\mathbf{r})\frac{\partial^2}{\partial x_{\alpha}\partial x_{\beta}}\phi_b(\mathbf{r}-\mathbf{r}_l).$$

Thus ΔE^{V} is given by Eq. (61e).

APPENDIX E

From Appendix D,

$$(\Delta E_d{}^{\mathrm{III}})_2+\Delta E_c{}^{\mathrm{III}} = -\tfrac{1}{2}\sum_{l,\beta}u_{\beta}{}^{l}\sum_{k,k'}n(k) \times\left\{M_{k'k}\int_{V_0(l)}d\mathbf{r}\,\psi_{k'}\frac{\partial}{\partial x_{\beta}}\psi_k{}^{*} - M_{kk'}\int_{V_0(l)}d\mathbf{r}\,\psi_k\frac{\partial}{\partial x_{\beta}}\psi_{k'}{}^{*}\right\}. \quad \text{(E1)}$$

Using the expression for $M_{k'k}$ given in Eq. (33a), we get

$$\begin{aligned}(\Delta E_d{}^{\mathrm{III}})_2+\Delta E_c{}^{\mathrm{III}} = {}&-\tfrac{1}{2}\sum_{k,k'}n(k)\sum_{l,l',\alpha,\beta}u_{\alpha}{}^{l}u_{\beta}{}^{l'}\frac{\hbar^2}{2m} \times\int_{V_0(l)}d\mathbf{r}\int_{V_0(l')}d\mathbf{r}'\left[\nabla_{\mathbf{r}}{}^{2}\psi_{k'}{}^{*}(\mathbf{r})\frac{\partial}{\partial x_{\alpha}}\psi_k(\mathbf{r})\right.\\ &\left.-\psi_{k'}{}^{*}(\mathbf{r})\nabla_{\mathbf{r}}{}^{2}\frac{\partial}{\partial x_{\alpha}}\psi_k(\mathbf{r})\right]\left[\psi_{k'}(\mathbf{r}')\frac{\partial}{\partial x_{\beta}{}'}\psi_k{}^{*}(\mathbf{r}')\right]\\ &-\left[\nabla_{\mathbf{r}}{}^{2}\psi_k{}^{*}(\mathbf{r})\frac{\partial}{\partial x_{\alpha}}\psi_{k'}(\mathbf{r})-\psi_k{}^{*}(\mathbf{r})\nabla_{\mathbf{r}}{}^{2}\frac{\partial}{\partial x_{\alpha}}\psi_{k'}(\mathbf{r})\right] \times\left[\psi_k(\mathbf{r}')\frac{\partial}{\partial x_{\beta}{}'}\psi_{k'}{}^{*}(\mathbf{r}')\right].\end{aligned} \quad \text{(E2)}$$

By summing over k' and using the completeness property of the $\psi_{k'}$ we may show that the first term vanishes unless $l=l'$. The second term may be transformed by means of the divergence theorem to yield

$$\begin{aligned}&-\tfrac{1}{2}\sum_{k,k'}n(k)\sum_{ll',\alpha\beta}u_{\alpha}{}^{l}u_{\beta}{}^{l'}\frac{\hbar^2}{2m}\int_{V_0(l)}d\mathbf{r}\int_{V_0(l')}d\mathbf{r}' \times\left[\nabla_{\mathbf{r}}{}^{2}\psi_k{}^{*}(\mathbf{r})\frac{\partial}{\partial x_{\alpha}}\psi_{k'}(\mathbf{r})-\psi_k{}^{*}(\mathbf{r})\nabla_{\mathbf{r}}{}^{2}\frac{\partial}{\partial x_{\alpha}}\psi_{k'}(\mathbf{r})\right]\\ &\times\left[\psi_{k'}{}^{*}(\mathbf{r}')\frac{\partial}{\partial x_{\beta}{}'}\psi_k(\mathbf{r}')\right]+\tfrac{1}{2}\sum_{k,k'}n(k)\sum_{ll',\alpha\beta}u_{\alpha}{}^{l}u_{\beta}{}^{l'}\frac{\hbar^2}{2m} \times\int_{V_0(l)}d\mathbf{r}\int_{S_0(l')}dS_{\beta}{}'\left[\nabla_{\mathbf{r}}{}^{2}\psi_k{}^{*}(\mathbf{r})\frac{\partial}{\partial x_{\alpha}}\psi_{k'}(\mathbf{r})\right.\\ &\left.-\psi_k{}^{*}(\mathbf{r})\nabla_{\mathbf{r}}{}^{2}\frac{\partial}{\partial x_{\alpha}}\psi_{k'}(\mathbf{r})\right]\psi_{k'}{}^{*}(\mathbf{r}')\psi_k(\mathbf{r}').\end{aligned} \quad \text{(E3)}$$

Now we may again use the completeness property of the $\psi_{k'}$ to show that the above expression also vanishes unless $l=l'$.

Thus $(\Delta E_d{}^{\mathrm{III}})_2+\Delta E_c{}^{\mathrm{III}}$ may be written as $-\frac{1}{2}\sum_{l\alpha\beta}\times u_{\alpha}{}^{l}u_{\beta}{}^{l}C$ and contributes only a constant to the dynamical matrix. The constant C may be absorbed into $\phi_{\alpha\beta}{}^{ll}$ which need not be calculated explicitly as discussed in Sec. V.