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General Theory of Pseudopotentials

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It has previously been shown that the energy levels of valence electrons in atoms, molecules, and solids can be calculated from a weak net effective pseudopotential V_p. In V_p most of the large negative potential energy of an electron, when inside the ion core of an atom, has been canceled against the large positive kinetic energy which the electron has there. It has recently been shown that there are several different forms which the pseudopotential can take. The theory is now developed from a different point of view, and it is shown that there exists an even wider class of pseudopotentials which all give the same valence energy levels. One of these, previously derived as an approximation, is now seen to be an exact form of the pseudopotential. Since it is much simpler and more convenient than other forms, its properties are investigated further with a view to its use for detailed numerical calculations. Finally, it is shown how the pseudopotential can be used not only for calculating valence energy levels, but also for the scattering of electrons by phonons and impurities in solids and by the disorder in liquid metals.

1. INTRODUCTION

It has recently been emphasized[1–4] that in an atom, molecule, or solid, there is almost complete cancellation between the large negative potential energy $V(\mathbf{r})$ felt by a valence electron when inside the core of an atom, and its large positive kinetic energy which is inherent in the oscillations of its wave function ψ_v there. Mathematically the cancellation can be demonstrated by showing that the wave equation

$$H\psi_v \equiv (T+V)\psi_v = E_v\psi_v \tag{1}$$

can be transformed into

$$(H+V_R)\phi_v \equiv (T+V+V_R)\phi_v = E_v\phi_v, \tag{2}$$

when V_R is a nonlocal repulsive potential which cancels off most of V, leaving a weak net potential $(V+V_R)$ which we shall refer to as the pseudopotential V_p. In (2), ϕ_v is a pseudo-wave function which is equal to ψ_v outside the atomic core, but inside the core has the oscillations of ψ_v removed; e.g., for a sodium atom the ϕ_{3s}, ϕ_{4s}, $\cdots$ functions, corresponding to the $3s$, $4s$, $\cdots$ valence levels, have the general shape of $1s$, $2s$, $\cdots$ wave functions with zero, one, $\cdots$ radial nodes.

Phillips and Kleinman,[1,2] also Antončík,[5] first showed that V_R could be defined by

$$V_R^{\mathrm{PK}}\phi_v = \sum_c (E_v - E_c)(\psi_c,\phi_v)\psi_c, \qquad (\psi_c,\phi) = \int \psi_c^*\phi\, dv, \tag{3}$$

which we shall call the PK theorem, where E_c, ψ_c are the eigenvalues and eigenfunctions of H with the quantum numbers of states in the core of the atom, i.e., $c=1s$, $2s$, $2p_x$, $2p_y$, $2p_z$ for sodium: in the case of a polyatomic system, we shall take the summation over c to include summing over all the atoms, and shall assume the ψ_c's from neighboring atoms do not overlap appreciably. Cohen and Heine[4] then showed that there are actually several forms which can be taken for V_R, in particular

$$\begin{aligned} V_p^{\mathrm{CH}}\phi &\equiv (V+V_R^{\mathrm{CH}})\phi \\ &= V\phi - \textstyle\sum_c(\psi_c,V\phi)\psi_c + \bar{V}\sum_c(\psi_c,\phi)\psi_c, \end{aligned} \tag{4}$$

where

$$\bar{V} = (\phi,\, V+V_R\phi)/(\phi,\phi). \tag{5}$$

Dropping the last term of (4), they suggested as an approximation

$$V_p^{\mathrm{A}}\phi \equiv (V+V_R^{\mathrm{A}})\phi = V\phi - \textstyle\sum_c(\psi_c,V\phi)\psi_c. \tag{6}$$

The present work was initiated when one of us (B. J. A.) noticed that (6) is not an approximation at all, but is still a valid form for V_p satisfying (2).[6] It is by far the simplest form of the pseudopotential that has been developed. In particular, it gets rid of the awkward term in $\bar{V}$ which can only be defined self-consistently in terms of the ϕ_v which one is trying to calculate. The importance of the form (6) is that it really turns the use of pseudopotentials from a qualitative or formal justification of the nearly free electron approximation and similar crude models,[4] into a useful method of doing quantitative calculations.

In Sec. 2 we shall state and prove what we call the general pseudopotential theorem. It exhibits the most general form that can be taken for V_R, containing (6), (3), and (4) as special cases. It also throws new light onto what happens to the core eigenstates of H when one transforms to the pseudopotential formalism, and

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* Supported by a Shirtcliffe Fellowship from the University of New Zealand, which is gratefully acknowledged.

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[1] J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[2] L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

[3] E. Antončík, J. Phys. Chem. Solids **10**, 314 (1959) and references given there.

[4] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961), hereafter referred to as I.

[5] E. Antončík (unpublished).

[6] Since completing this manuscript, we have noticed that the form (6) had previously been written down by F. Bassani and V. Celli [J. Phys. Chem. Solids **20**, 64 (1961)] using an incomplete form of the theorem of Sec. 2. There is otherwise no overlap with the present work.

the special role played here by the form V_R^{PK} (3) of V_R. Although one can generate an infinite number of valid forms of V_R, not all of them are equally useful insofar as they do not all produce equally rapid convergence if one expands ϕ_v in, say, a series of plane waves in the case of a metal. In Sec. 3, we shall therefore discuss, from this point of view, the ϕ^{A} generated by the use of our form V_R^{A} (6).

Finally, we shall discuss the transition probability for scattering. What we have in mind is the scattering of electrons by a distortion of a solid produced by a lattice vibration (electron-phonon interaction),[7] the scattering by an impurity atom in a solid such as gold in silver, and the scattering of electrons in a liquid metal when we start from a free-electron model and introduce the atoms as weak scatterers.[8] Although the PK theorem and its generalization only assert that the correct eigenvalues of H can be calculated from the pseudopotential V_p, it is superficially obvious[8] that V_p can also be used to calculate scattering matrix elements. However, it took Sham[7] a considerable amount of algebra to show that the particular case of the electron-phonon interaction is correctly given by the use of the particular form V_p^{PK}. One trouble is that V_R is not exactly a Hermitian operator, although, clearly, the resulting transition probability between two states of ϕ_{v1} and ϕ_{v2} must be the same in both directions. Furthermore, the ϕ_v's are no longer orthogonal, in general, nor is it completely obvious how they should be normalized. In view of these uncertainties, we shall show in Sec. 4 that scattering probabilities can be correctly calculated from the pseudopotential in any of its forms in all the situations mentioned above, and shall develop the correct formulas for handling them. In Sec. 5 we relate the calculation of scattering amplitudes in the pseudopotential formalism to that in the orthogonalized plane-wave formalism.

2. GENERAL PSEUDOPOTENTIAL THEOREM

Let us start by calculating the eigenvalues and eigenfunctions of $H+V_R$, where V_R is defined by

$$V_R\phi=\sum_c (F_c,\phi)\psi_c. \tag{7}$$

Here, the F_c are completely arbitrary functions. We shall denote the eigenvalues and eigenfunctions of H by E_n, ψ_n, writing $n=c$ or v if we want to restrict ourselves to core or valence states. The corresponding eigenvalues and eigenfunctions of the pseudo-Hamiltonian $H_p=H+V_R$ we shall denote by $\tilde{E}_n$, ϕ_n, again with $n=c$ or v

$$H_p\phi_n\equiv(H+V_R)\phi_n=\tilde{E}_n\phi_n. \tag{8}$$

Let us first consider the core states and expand ϕ_c in terms of the complete orthonormal set of functions ψ_n:

$$\phi_c=\sum_{c'}\alpha_{c'}\psi_{c'}+\sum_v \alpha_v\psi_v. \tag{9}$$

Substituting into (7) and (8), we obtain

$$\sum_{c'}\sum_{c''}[(E_{c'}-\tilde{E}_c)\delta_{c'c''}+(F_{c'},\psi_{c''})]\alpha_{c''}\psi_{c'} \\ +\sum_{c'}\sum_v \alpha_v(F_{c'},\psi_v)\psi_{c'}+\sum_v(E_v-\tilde{E}_c)\alpha_v\psi_v=0. \tag{10}$$

In this the coefficient of every ψ_n must vanish. Thus, unless there is some accidental degeneracy between $\tilde{E}_c$ and some E_v, we have that all $\alpha_v=0$. Thus, ϕ_c is a linear combination of the ψ_c's, and its energy $\tilde{E}_c$ is given by the secular equation

$$\det|(E_{c'}-\tilde{E}_c)\delta_{c'c''}+(F_{c'},\psi_{c''})|=0. \tag{11}$$

It should be noted that this discussion of "core" solutions of (8) is purely formal and is of no interest in discussing the real core states of the atom. However, these "core" solutions do exist and are relevant at three places below in discussing the valence levels.

We now calculate the valence states by expanding them similarly in terms of the ψ_n's:

$$\phi_v=\sum_c \alpha_c\psi_c+\sum_{v'}\alpha_{v'}\psi_{v'}. \tag{12}$$

Substituting into (7) and (8), we obtain

$$\sum_c\sum_{c'}[(E_c-\tilde{E}_v)\delta_{cc'}+(F_c,\psi_{c'})]\alpha_{c'}\psi_c+\sum_c(F_c,\psi_v)\alpha_v\psi_c \\ +(E_v-\tilde{E}_v)\alpha_v\psi_v+\sum_{v'\neq v}(E_{v'}-\tilde{E}_v)\alpha_{v'}\psi_{v'} \\ +\sum_{v'\neq v}\sum_c(F_c,\psi_{v'})\alpha_{v'}\psi_c=0. \tag{13}$$

From the coefficient of ψ_v, we have $\tilde{E}_v=E_v$. From the coefficient of $\psi_{v'}$ we have $\alpha_{v'}=0$ unless there is some degeneracy. Thus, ϕ_v has the form

$$\phi_v=\psi_v+\sum_c \alpha_c\psi_c, \tag{14}$$

where from (13) the α_c's are determined by the set of linear equations

$$\sum_{c'}[(E_c-E_v)\delta_{cc'}+(F_c,\psi_{c'})]\alpha_{c'}=-(F_c,\psi_v). \tag{15}$$

Comparison with (11) shows that (15) has a unique solution unless there is some accidental degeneracy between E_v and an $\tilde{E}_c$. Throughout this proof, if some degeneracy does occur, it results in a degree of arbitrariness in the wave functions which may, however, still be chosen in the form described above.

We have therefore the general pseudopotential theorem:—The pseudo-Hamiltonian $H_p=H+V_R$, where V_R is given by (7), has the same valence eigenvalues E_v as H does, the eigenfunctions being given by (14) and (15); the "core" eigenfunctions of H_p are linear combinations of the core eigenfunctions of H and their energies are given by (11). Moreover it is clear from the proof of the theorem that the essential property that V_R must have is that it projects any ϕ onto the space spanned by the ψ_c's. Since (7) is the most general operator of this type, (7) with arbitrary functions F_c represents the most general form for V_R.

Finally, we take the matrix element of (14) with ψ_c and obtain $\alpha_c=(\psi_c,\phi_v)$. Thus, we can write (14) in the

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[7] L. J. Sham, Proc. Phys. Soc. (London) **78**, 895 (1961).

[8] J. M. Ziman, Phil. Mag. **6**, 1013 (1961).

form

$$\phi_v = \psi_v + \textstyle\sum_c (\psi_c, \phi_v)\psi_c. \tag{16}$$

It is important to note that this does not imply any particular value of the α_c's; ϕ_v varies with α_c in such a way that (16) is automatically true for any α_c's. It really expresses the orthogonality of ψ_v and ψ_c, and cannot be taken as a full definition of ϕ_v in terms of ψ_v and the ψ_c's.[9]

If we now take

$$F_c = -V\psi_c \tag{17}$$

in (7), we obtain the Austin form $V_p{}^{\mathrm{A}}$ (6), which we have therefore proved to be a valid form for the pseudopotential. Similarly, the forms $V_R{}^{\mathrm{PK}}$ (3), $V_R{}^{\mathrm{CH}}$ (4), and other forms given in I are all seen to be special cases of (7). We can also take over from I the use of a model potential V_M which is completely open to choice; we have then for the pseudopotential

$$(V+V_R)\phi = V_M\phi + [(V-V_M)\phi - \textstyle\sum_c (\psi_c,\, (V-V_M)\phi)\psi_c]. \tag{18}$$

In I, it was rather implied that the core eigenstates somehow completely disappeared when one went to the pseudo-Hamiltonian form. This is now seen to be incorrect; indeed, we have in (11) derived an equation for the eigenvalues $\bar{E}_c$. However, it remains important for the practical application of pseudopotentials that the lowest valence states of H should become the lowest eigenstates of $H+V_R$, because one wants to set up, for instance, secular equations in terms of plane waves whose lowest eigenvalues converge to the E_v's and not to some lower core states. Thus, it becomes important where the $\bar{E}_c$ lie. In the case of the pseudopotential (6) we note that (11) becomes Hermitian and $\bar{E}_c$ real, and we have from the diagonal elements

$$\bar{E}_c \approx E_c - (\psi_c, V\psi_c) = (\psi_c, T\psi_c). \tag{19}$$

Here, T is the kinetic energy operator, and we have used

$$(T+V)\psi_c = E_c\psi_c. \tag{20}$$

The off-diagonal elements of (11) become $(\psi_c, T\psi_{c'})$ which are rather smaller because of the orthogonality of the ψ_c's. Now, very roughly,

$$(\psi_c, T\psi_c) \approx |E_c|. \tag{21}$$

We therefore have that the "core" levels $\bar{E}_c$ of $H+V_R{}^{\mathrm{A}}$ lie about as high up in the continuum as the real core levels E_c of H lie below the valence levels. However, if the outermost valence level is rather loosely bound, some care may be needed in calculating excited valence states in order not to pick up one of the spurious levels $\bar{E}_c$.

To get the form $V_R{}^{\mathrm{PK}}$ (3), we put in (7)

$$F_c = (E_{v0} - E_c)\psi_c, \tag{22}$$

where E_{v0} is the particular valence level one is wanting to calculate. It then follows from (11) or by direct substitution that all the ψ_c become eigenstates of $H+V_R{}^{\mathrm{PK}}$ with pseudo-energy $\bar{E}_c$ all equal to E_{v0}. The α_c in (14) can then be chosen arbitrarily because of the degeneracy. Note that this arbitrariness, first pointed out by Kohn,[9] applies only to the PK form of the pseudopotential.[4] If we denote by $\phi_v{}^X$ the pseudowave function obtained from a particular form $V_R{}^X$, then the arbitrariness means that any $\phi_v{}^X$ is automatically a $\phi_v{}^{\mathrm{PK}}$, and we have from (2), (16), (20), and (3)

$$\begin{aligned} V_R{}^X\phi_v{}^X &= (H+V_R{}^X)\phi_v{}^X - H\phi_v{}^X \\ &= E_v\phi_v{}^X - H\psi_v - \textstyle\sum_c(\psi_c,\phi_v{}^X)H\psi_c \\ &= E_v\psi_v + \textstyle\sum E_v(\psi_c,\phi_v{}^X)\psi_c - E_v\psi_v \\ &\qquad - \textstyle\sum E_c(\psi_c,\phi_v{}^X)\psi_c \\ &= \textstyle\sum (E_v - E_c)(\psi_c,\phi_v{}^X)\psi_c \\ &= V_R{}^{\mathrm{PK}}\phi_v{}^X. \end{aligned} \tag{23}$$

We can, therefore, regard V_R in two different ways. We can either regard V_R as always being the same operator, a particular form then being obtained by defining a particular set of α_c's, and thus a particular representation of the operator. This is rather the approach used in I, where we fix the representation by fixing the matrix elements $(\psi_c, V_R\phi)$, as in Eqs. (21) and (22) of I. Alternatively we can regard the various forms as different operators all satisfying (2), with $V_R{}^{\mathrm{PK}}$ having some special properties because of the degeneracy between the $\bar{E}_c$'s and E_v, which is more our present attitude.

3. SMOOTHNESS OF $\phi_v{}^{\mathrm{A}}$

As is well known in the orthogonalized plane-wave (OPW) method of calculating band structures in solids, one can in (14) eliminate the radial oscillations of ψ_v inside the core by choosing the α_c appropriately.[4,10] Indeed the whole purpose of using pseudopotentials is to work in terms of functions ϕ_v which are quite smooth inside the core, so that in the case of solids or liquid metals, for instance, they can be represented well by only a few plane waves. We therefore have to ask, if we use the particular form $V_p{}^{\mathrm{A}}$ (6) of the pseudopotential, how smooth does the resulting function $\phi_v{}^{\mathrm{A}}$ turn out to be? In view of the importance of this particular form, we shall approach the question from two different angles.

We first note that $V_p{}^{\mathrm{A}}$ can be generated from a variational principle in the manner of I. We shall omit the detailed derivation, since it follows closely Eqs. (17) to (23) of I. The quantity to vary is

$$-(\phi,\, (V+V_R)\phi) \equiv (\phi, T\phi) - E_v(\phi,\phi); \tag{24}$$

i.e., the $\phi_v{}^{\mathrm{A}}$ given by $V_p{}^{\mathrm{A}}$ is such that it automatically minimizes (24). This is not the usual form of a varia-

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[9] See footnote 27 of I.

[10] C. Herring, Phys. Rev. **57**, 1169 (1940).

tional principle as used in I, because we have not divided by the normalization (ϕ,ϕ). We assume here that ϕ has the form (14), i.e., that ϕ is so normalized that its projection on ψ_v is unity when ψ_v is normalized to one. Thus, from (14) or (16) ϕ is normalized to

$$(\phi,\phi)=1+\sum_c|\alpha_c|^2=1+\sum_c|(\psi_c,\phi)|^2, \tag{25}$$

where the second term is typically about 0.1. Since it is so small, minimizing (24) is very nearly the same as minimizing

$$\bar{T}=(\phi,T\phi)/(\phi,\phi)=\int|\nabla\phi|^2dv/(\phi,\phi). \tag{26}$$

Now, as mentioned in I, minimizing (26) generates the smoothest ϕ possible, and thus the ϕ^{A} generated by $V_p{}^{\mathrm{A}}$ is very nearly the smoothest ϕ.

We can compare ϕ^{A} with the smoothest ϕ more quantitatively as follows. From (2), (5), and (25) we have

$$\bar{T}+\bar{V}=E_v=\text{const}, \tag{27}$$

so that minimizing $\bar{T}$ (26) is the same as maximizing $\bar{V}$. In I the latter condition was used to generate $V_p{}^{\mathrm{CH}}$ (4). We have therefore that the ϕ^{CH} given by $V_p{}^{\mathrm{CH}}$ is the smoothest ϕ possible, the smoothness being measured by the kinetic energy $\bar{T}$ (26). Now the difference between $V_p{}^{\mathrm{A}}$ (6) and $V_p{}^{\mathrm{CH}}$ (4) is just the small $\bar{V}$ term contained in (4), and the increase in kinetic energy produced by dropping it can be calculated by perturbation theory. We put

$$\phi_v{}^{\mathrm{A}}=\phi_v{}^{\mathrm{CH}}+\sum_c\beta_c\psi_c \tag{28}$$

into (2), (4), and (6), giving

$$(E_c-E_v)\beta_c-\sum_{c'}(\psi_c,V\psi_{c'})\beta_{c'}=\bar{V}(\psi_c,\phi_v{}^{\mathrm{CH}}). \tag{29}$$

By way of a very rough approximation, we obtain from the diagonal elements of the secular equation (29)

$$\beta_c\approx\frac{\bar{V}(\psi_c,\phi_v{}^{\mathrm{CH}})}{(\psi_c,T\psi_c)-E_v}. \tag{30}$$

The increase ΔT in kinetic energy is to second order

$$\begin{aligned}\Delta T&=\frac{(\phi^{\mathrm{A}},T\phi^{\mathrm{A}})}{(\phi^{\mathrm{A}},\phi^{\mathrm{A}})}-\bar{T}\\&=\sum_{c,c'}\frac{\beta_c{}^*\beta_{c'}(\psi_c,T\psi_{c'})}{(\phi^{\mathrm{CH}},\phi^{\mathrm{CH}})}-\sum_c\bar{T}\frac{|\beta_c|^2}{(\phi^{\mathrm{CH}},\phi^{\mathrm{CH}})}.\end{aligned} \tag{31}$$

There are no first-order terms in ΔT, because $\bar{T}$ is the minimum value of (25). In practice, the extra waviness of ϕ^{A} corresponding to ΔT results, of course, in a slower convergence if one is expanding ϕ in some series of functions. By way of illustration, we have estimated the magnitude of the effect for the levels Γ_1, W_1, $W_2{}'$, and W_3 in the band-structure calculation of solid aluminum.[11] Putting (21) into (30) and (31), we obtain $\Delta T=0.001$, 0.01, 0.001, and 0.002 rydberg as regards order of magnitude for these levels. This is comparable with the ordinary contributions of the higher states in the secular equation,[12] and in each case is less than 1% of the amount of kinetic energy $(\phi,V_R\phi)/(\phi,\phi)$ which has been canceled off by V_R. We conclude that for practical purposes ϕ^{A} is not seriously less smooth than ϕ^{CH}, the smoothest ϕ.

The usefulness of $V_p{}^{\mathrm{A}}$ can also be gauged from a direct comparison with the OPW method[10] in solids. We first introduce a slight modification of (6), obtained by putting V_M equal to a constant V_0 in (18):

$$V_p{}^{\mathrm{A}}\phi=V\phi-\sum_c(\psi_c,(V-V_0)\phi)\psi_c. \tag{32}$$

It is now invariant to a change in the zero from which V is measured, which (6) is not. We then set up a secular equation for $H_p(=T+V_p{}^{\mathrm{A}})$ in terms of plane waves with wave vectors $\mathbf{k}$ and $\mathbf{k}+\mathbf{g}_n$, where the $\mathbf{g}_n$'s are the reciprocal lattice vectors, and use this to calculate the energy of the lowest state $E_{\mathbf{k}}$. The use of (32) results, of course, in a non-Hermitian secular equation, and it is important to note that in first-order perturbation theory the coefficient of the wave $\mathbf{k}+\mathbf{g}$ mixed into the lowest state is given by the matrix element $(H_p)_{\mathbf{k}+\mathbf{g},\mathbf{k}}$ from the first column, not by $(H_p)_{\mathbf{k},\mathbf{k}+\mathbf{g}}$ from the first row. We have

$$\begin{aligned}(H_p)&{}_{\mathbf{k}+\mathbf{g},\mathbf{k}}\\&=V_{\mathbf{k}+\mathbf{g},\mathbf{k}}-\sum_c(\mathrm{PW}\mathbf{k}+\mathbf{g},\psi_c)(\psi_c,(V-V_0)\,\mathrm{PW}\mathbf{k})\\&=V_{\mathbf{k}+\mathbf{g},\mathbf{k}}+\sum_c(\mathbf{k}^2+V_0-E_c)(\mathrm{PW}\mathbf{k}+\mathbf{g},\psi_c)(\psi_c,\mathrm{PW}\mathbf{k}),\end{aligned} \tag{33}$$

where we have used $V=H-T$ and (20). The corresponding element in the OPW calculation is

$$\begin{aligned}(\mathrm{OPW}\mathbf{k}+\mathbf{g},(H-E_{\mathbf{k}})\,\mathrm{OPW}\mathbf{k})=V_{\mathbf{k}+\mathbf{g},\mathbf{k}}&\\+\sum_c(E_{\mathbf{k}}-E_c)(\mathrm{PW}\mathbf{k}+\mathbf{g},\psi_c)(\psi_c,\mathrm{PW}\mathbf{k}).&\end{aligned} \tag{34}$$

Comparing this with (32), we see that they become identical if we choose

$$V_0=E_{\mathbf{k}}-\mathbf{k}^2. \tag{35}$$

In practice, if we put

$$V_0=E_{k=0}, \tag{36}$$

then (35) is very nearly satisfied for all $\mathbf{k}$, at least in comparison with the E_c in (33), (34). We conclude, therefore, that the secular equation for H_p in terms of plane waves, using (32) and (34), shows the same convergence to a first approximation as the secular equation of the orthogonalized plane wave method. It has the advantage over the latter that the required energy $E_{\mathbf{k}}$ does not appear in the off-diagonal elements, but the disadvantage that the equation is not Hermitian (see also below).

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[11] V. Heine, Proc. Roy. Soc. (London) **A240**, 361 (1957).
[12] V. Heine, Proc. Roy. Soc. (London) **A240**, 354 (1957).

4. TRANSITION PROBABILITIES

The transition probability per unit time from a state ψ_1 to a state ψ_2 is, as usual,

$$1/\tau=(2\pi/\hbar)|W_{21}|^2 n(E), \tag{37}$$

where W_{21} is the scattering amplitude and $n(E)$ the density of states, and where $1/\tau$ and $n(E)$ are expressed per unit solid angle or other suitable angular range around the direction of ψ_2. Since the energy eigenvalues E_v of the Hamiltonian H and of the pseudo-Hamiltonian H_p are the same, $n(E)$ is also the same and we need only concern ourselves with the calculation of W_{21}.

We first prove the scattering amplitude theorem: the scattering amplitude for any system of atoms is the same when calculated from V or V_p, provided the pseudo wave functions are normalized as in (25), i.e., normalized so that the projection of ϕ_v on ψ_v is unity when ψ_v is normalized to unity. In the case of a single atom, the scattering amplitude is defined by taking an incident plane wave at infinity and constructing a wave function which at large distances behaves like

$$\psi \rightarrow e^{i\mathbf{k}_1\cdot\mathbf{r}}+f(\theta,\phi)e^{ik_1 r}/r, \tag{38}$$

where $f(\theta,\phi)$ then gives the scattering amplitude. Here ψ is an eigenfunction of H satisfying the scattering type of boundary conditions, so that we can apply the pseudopotential theorem to it and construct a corresponding ϕ which is an eigenfunction of H_p. This ϕ is the wave function which one would obtain if one did a scattering calculation with V_p, since it satisfies the required boundary conditions. From (14), ϕ and ψ are identical outside the range of the ψ_c, and thus give the scattering amplitude for an isolated atom. The same argument can now be applied to the scattering by one or more atoms in a solid or liquid, or in a solid disturbed by a phonon, or any other rearrangement of atoms. In this case, the incident wave is a Bloch function of the pure solvent or undisturbed solid. The scattering is defined by constructing an eigenfunction ψ of H with boundary conditions (38) for the scattered wavelet emanating from each atom. This is not yet an exact eigenfunction of H because it only includes single scattering: one really has to go on to take the scattered wavelets and scatter them in turn by the atoms they hit, and so on. The point is that at each stage there is a corresponding function ϕ derivable from H_p, which is the same as ψ in the "free" region between the cores, because we have previously shown that the scattered wavelets from each individual atom are the same when calculated from H or H_p. In order to get the flux of electrons right, it is clearly necessary to normalize the ϕ so that ψ and ϕ are identical in the region between the cores, i.e., according to (25), which proves the theorem.

We therefore wish to calculate the scattering produced by a change in the pseudopotential δV_p due to inserting, removing, substituting, or displacing atoms. As shown in I and in Sec. 3, V_R can be chosen so that V_p is a weak potential. Hence, δV_p is also weak and we can use perturbation theory to calculate the scattering by it. The kind of situation we have in mind is, for instance, gold atoms dissolved in silver. Here the actual change of potential δV is large, so large, of course, that it results in an extra radial node in the wave function, and this would render a perturbation calculation based on δV practically useless. However, the actual scattering of electrons by the gold atoms is small, corresponding to a small δV_p in which the change in the number of radial nodes has all been canceled off. Thus, we wish to calculate the scattering amplitude W_{21} of δV_p between two pseudostates ϕ_1 and ϕ_2 of the unperturbed system. This is not simply the matrix element $(\phi_2,\delta V_p\phi_1)$ because the ϕ_v's do not form an orthonormal set. We define the reciprocal functions ϕ^n with the property

$$(\phi^n,\phi_m)=\delta_{nm}. \tag{39}$$

In terms of these, the first-order perturbation expansion is easily verified to be

$$\phi_1(\text{perturbed})=\phi_1+\sum_{n\neq 1}\frac{(\phi^n,\delta V_p\phi_1)}{E_1-\tilde{E}_n}\phi_n, \tag{40}$$

where we have used $\tilde{E}_n$ because the summation runs over all core states with $\tilde{E}_c\neq E_c$ as well as over the valence states. The scattering amplitude is therefore[13]

$$W_{21}=(\phi^2,\delta V_p\phi_1). \tag{41}$$

It is straightforward but tedious to construct the set ϕ^n systematically from (39), so we shall simply verify by inspection from (14), (39), and from ϕ_c being a linear combination of the ψ_c's, that ϕ^v is in fact just ψ_v. Thus from (16), (41) becomes

$$W_{21}=(\phi_2,\delta V_p\phi_1)-\textstyle\sum_c(\phi_2,\psi_c)(\psi_c,\delta V_p\phi_1), \tag{42}$$

which is our final result for the scattering amplitude to first order in δV_p. In practice, the second term in (42) will be very small, particularly if one uses the form $V_p{}^A$, because then V_p and δV_p are already as near zero as possible over the region of the ψ_c's.

When δV is itself small enough to be treated by first-order perturbation theory, we have

$$W_{21}=(\psi_2,\delta V\psi_1), \tag{43}$$

and this should reduce algebraically to (42) without having to appeal to the general arguments used in proving the scattering amplitude theorem. The required manipulations turn out to be somewhat tortuous, involving as they do also the first-order changes in ψ_c and in V_R, and we record them in the Appendix as a check on the general theory.

As it stands, (42) is not obviously Hermitian between ϕ_2 and ϕ_1. Indeed, V_R (7) itself is not, in general, a Hermitian operator. However, we shall prove that it

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[13] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon Press, New York, 1958), pp. 147, 149.

has the Hermitian property

$$(\phi_1, V_R\phi_2) = (\phi_2, V_R\phi_1)^*, \tag{44}$$

if ϕ_1 and ϕ_2 are pseudo-wave functions belonging to the same energy E, which we take to lie in the continuum as in a scattering problem. We can expand ϕ_1, ϕ_2 about each scattering atom in terms of spherical harmonics Y_{lm}

$$\begin{aligned} \phi_1 &= \textstyle\sum_{lm} A_{1,lm} Y_{lm}(\theta,\phi) f_{lm}(r; E_1), \\ \phi_2 &= \textstyle\sum_{lm} A_{2,lm} Y_{lm}(\theta,\phi) f_{lm}(r; E_2), \end{aligned} \tag{45}$$

or in terms of Kubic harmonics or other symmetry functions as appropriate. Here $Y_{lm}(\theta,\phi) f_{lm}(r; E)$ is the solution of the pseudo-Schrödinger equation with symmetry Y_{lm} and energy E, integrated outwards from $\phi=$finite at $r=0$. Similarly in V_R (7), the ψ_c can be sorted out according to the symmetry of the system, namely, the Y_{lm} in our example, and then (ϕ_2, ψ_c) picks out from (45) only the term with the same l and m. If V_R is to preserve the spherical or other symmetry of the system, then F_c in (7) has to have the same symmetry properties as ψ_c and (F_c, ϕ_1) picks out the corresponding term from (45). We have, therefore,

$$\begin{aligned} (\phi_2, V_R\phi_1) &= \textstyle\sum_{lm} A_{2,lm}^* A_{1,lm} \\ &\times \textstyle\sum_c (f_{lm}(r; E_2) Y_{lm}, \psi_{clm})(F_{clm}, Y_{lm} f_{lm}(r; E_1)), \end{aligned} \tag{46}$$

from which (44) immediately follows if and only if $E_1=E_2$, in general. If the symmetry is other than spherical, the summation in (45) is over all the components of all the irreducible representations, and the orthogonality of the representations preserves the result as before.[14] The same reasoning can be applied to the scattering amplitude (42). Since in an elastic scattering problem ϕ_1 and ϕ_2 always do have the same energy, we obtain therefore the property

$$W_{12} = W_{21}^* \tag{47}$$

required by the principle of microscopic reversibility.

Incidentally, the original PK form (3) of V_R is rather ambiguous in regard to Hermiticity. V_R^{PK} is a completely Hermitian operator if we regard E_v as a fixed parameter, for instance, the energy of some definite level which is to be calculated. Thus, if we use $H+V_R^{\mathrm{PK}}$ to set up a secular equation for E_v in terms of plane waves, we get[4] the OPW secular equation which is Hermitian. However, in general, a more consistent interpretation of V_R^{PK} as in (23) and in I would be that E_v refers to the energy of the ϕ following on the right. In that case, V_R^{PK} is not Hermitian although we again have the property (44) if $E_1=E_2$.

5. RELATION TO OPW CALCULATION

There is a close connection between the pseudopotential approach and the OPW method which has been mentioned above and elsewhere[1–4] as far as the determination of energy levels and eigenfunctions is concerned. The ideas of OPW'S can also be applied to calculating scattering amplitudes,[7,15,16] and we can compare this approach here with the results of Sec. 4. Consider again the case of scattering by a small concentration of gold atoms dissolved in silver. We start by doing a band-structure calculation for pure silver and obtain the conduction-band wave function ψ_v. Using (14), (16) we can construct from each ψ_v a corresponding smooth function ϕ_v at each of the atomic sites where we are going to substitute gold atoms; if the band-structure calculation is done using the OPW method, ϕ appears automatically as a linear combination of some plane waves. We have

$$\phi_v = \psi_v + \textstyle\sum_c (\psi_{c,\mathrm{Ag}}, \phi_v) \psi_{c,\mathrm{Ag}}, \tag{48}$$

where the summation includes summing over the sites of interest. We now substitute the gold atoms, and using (14), (16) again, we insert into ϕ the atomic-like oscillations appropriate to gold, which gives functions

$$\bar{\psi}_v = \phi_v - \textstyle\sum_c (\psi_{c,\mathrm{Au}}, \phi_v) \psi_{c,\mathrm{Au}}. \tag{49}$$

These are Bloch-like travelling waves with a single direction, but with the appropriate oscillations at each silver or gold atom. An electron is not scattered strongly by the gold atoms so that it has a long mean free path, and speaking pictorially we can say that $\bar{\psi}_v$ is the on-going unscattered part of the wave function. It is the $\bar{\psi}_v$'s that we use as a basis set if, for instance, we want to set up a Boltzmann equation for the electrons. Clearly, the $\bar{\psi}_v$'s are not eigenfunctions of the system, nor are they exactly orthogonal, and to obtain the scattering we have to calculate the effect of the full Hamiltonian H on $\bar{\psi}_v$. Using the expansion

$$\psi(t) = \textstyle\sum_v a_v(t) \bar{\psi}_v \exp(-iH_{vv}t/\hbar), \tag{50}$$

where H_{vv} is the diagonal element of H with respect to $\bar{\psi}_v$, we obtain for the scattering amplitude

$$W_{21} = (\bar{\psi}_2, (H - H_{11}) \bar{\psi}_1) \tag{51}$$

to first order in the off-diagonal elements of H and in the overlap. From (49) and (3), we obtain

$$\begin{aligned} (\bar{\psi}_2, (H-E)\bar{\psi}_1) &= (\phi_2, (H_0-E)\phi_1) + (\phi_2, V_{\mathrm{Au}}\phi_1) \\ &\quad + \textstyle\sum_c (E - E_{c,\mathrm{Au}})(\phi_2, \psi_{c,\mathrm{Au}})(\psi_{c,\mathrm{Au}}, \phi_1) \\ &= (\phi_2, (H_0-E)\phi_1) + (\phi_2, V_{p,\mathrm{Au}}^{\mathrm{PK}}\phi_1), \end{aligned} \tag{52}$$

where H_0 includes the kinetic energy and the potential energy at the unreplaced silver atoms, and V_{Au} and $V_{p,\mathrm{Au}}^{\mathrm{PK}}$ refer to all the replaced sites. Similarly, from

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[14] V. Heine, *Group Theory in Quantum Mechanics* (Pergamon Press, New York, 1960), pp. 42, 121.

[15] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. **8**, 173 (1959).

[16] This approach has also been talked about for some years among other people familiar with OPW's. We include here its application to impurity scattering because of its relation to Sec. 4 and because this application does not appear to have been set down before, without any claim to priority of invention.

(48) we have

$$0=(\psi_2,\ (H_{\mathrm{Ag}}-E)\psi_1)$$
$$=(\phi_2,\ (H_0-E)\phi_1)+(\phi_2,V_{p,\mathrm{Ag}}{}^{\mathrm{PK}}\phi_1), \tag{53}$$

where the whole expression is zero because ψ_2 and ψ_1 are eigenfunctions of the Hamiltonian H_{Ag} in pure silver. Substracting (53) from (52) and putting $E_1=E_2=H_{11}$, we obtain finally from (51)

$$W_{21}=(\phi_2,\ (V_{p,\mathrm{Au}}{}^{\mathrm{PK}}-V_{p,\mathrm{Ag}}{}^{\mathrm{PK}})\phi_1), \tag{54}$$

which is very similar to (42). The difference is that the small second term of (42) does not appear in this formulation, and that in (54) it is always the PK form of the pseudopotential that appears because we have used an OPW approach. The difference persists even if we use the PK pseudopotential in (42); this is due to the slight ambiguity in defining what one means by the on-going part of the wave function or the unscattered basis states, when these are not exact eigenfunctions (in the ψ form) of any Hamiltonian. We can apply (54) to scattering in a liquid metal[15] by taking an empty lattice as the unperturbed system and inserting the atoms. We obtain

$$W_{21}=(\phi_2,V_p{}^{\mathrm{PK}}\phi_1), \tag{55}$$

with V_p including all the atoms. (55) is now identical with (42) because there are no ψ_c's of the unperturbed system. Analogous results can be derived for electron-phonon scattering.[7]

APPENDIX

We wish to show that (42) reduces to (43) when δV is small. Let us subtract the expression (42) from (43), writing the difference as X which we want to show identically zero. Substituting (16) in (43), we have

$$\begin{aligned}X=-(\phi_2,\delta V_R\phi_1)&+\textstyle\sum_c(\phi_2,\psi_c)(\psi_c,\delta V_R\phi_1)\\&-\textstyle\sum_c(\phi_2,\delta V\psi_c)(\psi_c,\phi_1)\\&+\textstyle\sum_{c,c'}(\phi_2,\psi_c)(\psi_c,\delta V\psi_{c'})(\psi_{c'},\phi_1).\end{aligned} \tag{A1}$$

From (7) we have

$$\delta V_R\phi=\textstyle\sum_c(F_c,\phi)\delta\psi_c+\sum_c(\delta F_c,\phi)\psi_c, \tag{A2}$$

which we substitute into (A1), giving

$$\begin{aligned}X=-\textstyle\sum_c(\phi_2,\delta\psi_c)(F_c,\phi_1)&+\textstyle\sum_{c,c'}(\phi_2,\psi_c)(\psi_c,\delta\psi_{c'})(F_{c'},\phi_1)\\&-\textstyle\sum_c(\phi_2,\delta V\psi_c)(\psi_c,\phi_1)\\&+\textstyle\sum_{c,c'}(\phi_2,\psi_c)(\psi_c,\delta V\psi_{c'})(\psi_{c'},\phi_1).\end{aligned} \tag{A3}$$

From (7) and (23) we have

$$(F_c,\phi_1)=(E_1-E_c)(\psi_c,\phi_1), \tag{A4}$$

which substituted into (A3) gives

$$\begin{aligned}X=-\textstyle\sum_c&(\phi_2,\delta\psi_c)(E_1-E_c)(\psi_c,\phi_1)\\&+\textstyle\sum_{c,c'}(\phi_2,\psi_c)(\psi_c,\delta\psi_{c'})(E_1-E_{c'})(\psi_{c'},\phi_1)\\&-\textstyle\sum_c(\phi_2,\delta V\psi_c)(\psi_c,\phi_1)\\&\qquad+\textstyle\sum_{c,c'}(\phi_2,\psi_c)(\psi_c,\delta V\psi_{c'})(\psi_{c'},\phi_1).\end{aligned} \tag{A5}$$

$\delta\psi_{c'}$ is given by ordinary perturbation theory as

$$\delta\psi_{c'}=\textstyle\sum_{n\neq c'}(\psi_n,\delta V\psi_{c'})\psi_n/(E_{c'}-E_n), \tag{A6}$$

which gives

$$\begin{aligned}(\psi_c,\delta\psi_{c'})&=0 &&\text{if}\quad c=c',\\&=(\psi_c,\delta V\psi_{c'})/E_{c'}-E_c, &&\text{if}\quad c\neq c'.\end{aligned} \tag{A7}$$

From (16) we have

$$\phi_2=\psi_2+\textstyle\sum_{c'}(\psi_{c'},\phi_2)\psi_{c'}, \tag{A8}$$

which combined with (A6) gives

$$\begin{aligned}(\phi_2,\delta\psi_c)=&[(\psi_2,\delta V\psi_c)/(E_c-E_2)]\\&+\textstyle\sum_{c'\neq c}(\phi_2,\psi_{c'})(\psi_{c'},\delta V\psi_c)/(E_c-E_{c'}).\end{aligned} \tag{A9}$$

We now substitute (A9) into the first term of (A5), (A7) into the second term, and (A8) into the third term. If we then put $E_1=E_2$, all the pieces will be seen to cancel out, which proves our results.