Solution of Multiple Scattering by Finite Iteration

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We propose an iterative nonlinear solution to the general potential scattering problem in quantum mechanics. It is illustrated by the case of N_I localized scatterers of arbitrary strengths V_j located at arbitrary points R_j in an infinite lattice, for which we obtain the complete set of bound and scattering states. The numberical evaluation is estimated to take $O(N_I)$ steps as opposed to $O(N_I^3)$ steps by conventional matrix inversion.

Scattering theory, as traditionally expressed in the derivation and solution of the equation[1]

$$\psi(\vec{r}) = \eta_E \psi^{(0)}(\vec{r}) - \int G_E^{(0)}(\vec{r}', \vec{r}) V(\vec{r}') \psi(\vec{r}') d^3 r' \tag{1}$$

with $\eta_E = 1$ for E in the continuum and 0 for bound states, is generally intractable unless the potential is weak or has some high symmetry. For an arbitrary potential where the usual[1] expansions are inadequate and for which no simplifying symmetry is ascertained, I propose the following nonlinear, nonperturbative approach. The idea is to solve for the contribution from a small neighborhood $\Delta\Omega$ of each individual point where $V(\vec{r}')$ differs from zero, one point at a time. For example, starting at a specific $\vec{r}_0$ one would first consider

$$\psi(\vec{r}) = \psi^{(0)}(\vec{r}) - G_E^{(0)}(\vec{r}_0, \vec{r}) V(\vec{r}_0) \psi(\vec{r}_0) \Delta\Omega ,$$

which has the explicit solution

$$\psi^{(\vec{r}_0)}(\vec{r}) \equiv \psi(\vec{r}) = \psi^{(0)}(\vec{r}) - \frac{\Delta\Omega V(\vec{r}_0) G_E^{(0)}(\vec{r}_0, \vec{r}) \psi^{(0)}(\vec{r}_0)}{1 + G_E^{(0)}(\vec{r}_0, \vec{r}_0) V(\vec{r}_0) \Delta\Omega} , \tag{2}$$

and use this as the input at the next point $\vec{r}_1$

$$\psi^{(\vec{r}_0, \vec{r}_1)}(\vec{r}) = \psi^{(\vec{r}_0)}(\vec{r}) - \frac{\Delta\Omega V(\vec{r}_1) G_E^{(1)}(\vec{r}_1, \vec{r}) \psi^{(\vec{r}_0)}(\vec{r}_1)}{1 + G_E^{(1)}(\vec{r}_1, \vec{r}_1) V(\vec{r}_1) \Delta\Omega} , \tag{3}$$

in which there appears a new Green's function $G^{(1)}$ constructed with the eigenfunctions (2) and thus incorporating $V(\vec{r}_0)$. This procedure is then iterated, but it presents some difficulties. In addition to the scattering states there may appear bound states which must be computed separately. If we proceed to the limit $\Delta\Omega \to 0$, the number of points at which we must iterate becomes infinite. A proper formulation undoubtedly involves differential quantities such as $\partial\psi/\partial V$ at each point. Finally, the ultraviolet divergence of $G(\vec{r}, \vec{r})$ in two, three, or more dimensions necessitates a high-energy cutoff, which may be allowed to go to infinity only at the end of the calculations. At the present time I do not know how to circumvent these difficulties, which appear to provide many opportunities for further investigation. Nevertheless the solid-state analog to this problem is completely and explicitly solvable by such an iterative technique, as I now show.

We consider a simplified case, where electrons are confined to a single energy band of a solid with $N = \infty$ atoms, with N_I arbitrarily placed localized scatterers diffracting the electron waves. We shall obtain the exact eigenstates by a succession of N_I rotations of the Hilbert space. The model incorporates two important simplifications: First, the finite bandwidth of Bloch energies ϵ_k confined to a single band ensures that the Green's functions are free of ultraviolet divergences, obviating the need for an artificial cutoff. Second, the discrete nature of point scatterers enables us to terminate the process after a denumerable N_I steps.

We recall the few facts and the notation which are almost all the reader will have to know of solid

state theory.[2] Within each band there exist Wannier functions $\varphi(\vec{r}-\vec{R}_j)$ about each atom, $j=1,2,\ldots,N$. For our purposes, these N basis functions are complete. The Bloch states are the following:

$$\psi_{\vec{k}}^{(0)}(\vec{r}) = N^{-1/2}\sum_{j=1}^{N}\exp(i\vec{k}\cdot\vec{R}_j)\varphi(\vec{r}-\vec{R}_j) \tag{4}$$

for each band, with the N values of $\vec{k}$ lying in the first Brillouin zone (BZ). The Bloch states are the eigenfunctions of the perfect-crystal Hamiltonian H_0. We denote the above amplitudes $f_{\vec{k}}^{(0)}(\vec{R}_j) = N^{-1/2}\exp i\vec{k}\cdot\vec{R}_j$ the "Bloch amplitudes." Following Slater and Koster[3] we now introduce the N_I localized, pointlike, in-band, scattering centers with matrix elements

$$V_{\vec{k},\vec{k}'}^{(N_I)} = N^{-1}\sum_{j=1}^{N_I} V_j \exp[-i(\vec{k}-\vec{k}')\cdot\vec{R}_j], \tag{5}$$

in the Bloch representation. V_j and $\vec{R}_j$ are the arbitrary strengths and positions of the defects. After the first n of these have been taken into account, i.e., after $H^{(n)} = H_0 + V^{(n)}$ has been exactly diagonalized, the eigenfunctions are again developed in the set of Wannier functions

$$\psi^{(n)}(\vec{r}) = \sum_{j=1}^{N} f_{\vec{k}}^{(n)}(\vec{R}_j)\varphi(\vec{r}-\vec{R}_j), \tag{6}$$

with $\vec{k}$ a quantum index which must now span a number $Q^{(n)}$ of bound states[4] in addition to the continuum of scattering solutions. The matrix elements of the $(n+1)$th local scatterer, expressed in the new eigenfunctions (6) rather than in the primitive Bloch representation, are of the form

$$V_{n+1} f_{\vec{k}}^{(n)*}(\vec{R}_{n+1}) f_{\vec{k}}^{(n)}(\vec{R}_{n+1}), \tag{7}$$

where the $f_{\vec{k}}$'s in the continuum are $O(N^{-1/2})$ like the Bloch amplitudes, whereas the amplitudes of the $Q^{(n)}$ discrete states are $O(1)$. Scattering by the separable potential (7) is solvable in closed form, and I now give the results. There are $Q^{(n+1)}$ bound states, the energies of which are the roots $E_\alpha^{(n+1)}$ of the transcendental equation (we write E_α for $E_\alpha^{(n+1)}$ for clarity)

$$1 + V_{n+1} S^{(n)}(E_\alpha) = 0, \quad \alpha = 1, 2, \ldots, Q^{(n+1)}, \tag{8}$$

in which

$$S^{(n)}(E) \equiv \sum_{\vec{k}} \frac{|f_{\vec{k}}^{(n)}(\vec{R}_{n+1})|^2}{\epsilon_{\vec{k}} - E} = \sum_{\alpha=1}^{Q^{(n)}} \frac{|f_\alpha^{(n)}(\vec{R}_{n+1})|^2}{E_\alpha^{(n)} - E} + \int_{BZ} \frac{d^3k\, P_{\vec{k}}(\vec{R}_{n+1})}{\epsilon_{\vec{k}} - E}, \tag{9}$$

with $P_{\vec{k}}(\vec{R}_{n+1}) = [N/(2\pi)^3]\,|f_{\vec{k}}^{(n)}(\vec{R}_{n+1})|^2$. Thus, $S^{(n)}(E)$ has a branch cut on the real axis corresponding to the Bloch bandwidth, plus isolated poles at the $Q^{(n)}$ bound states of $H^{(n)}$. As the new roots $E_\alpha^{(n+1)}$ of (8) interlace the previous $E_\alpha^{(n)}$, their number must at most differ by one, i.e., $Q^{(n+1)} = Q^{(n)} \pm (1 \text{ or } 0)$, depending on the signs, strengths, and positions of the defects relative to one another.[4] The $Q^{(n+1)}$ bound states of (8) are easily obtained, and one finds their amplitudes at an arbitrary $\vec{R}$:

$$\begin{aligned} f_\alpha^{(n+1)}(\vec{R}) &= \left[\frac{\partial S^{(n)}(E_\alpha)}{\partial E_\alpha}\right]^{-1/2} \sum_{\vec{k}} \frac{f_{\vec{k}}^{(n)*}(\vec{R}_{n+1}) f_{\vec{k}}^{(n)}(\vec{R})}{\epsilon_{\vec{k}} - E_\alpha} \\ &= \left[\frac{\partial S^{(n)}(E_\alpha)}{\partial E_\alpha}\right]^{-1/2} G^{(n)}(\vec{R}_{n+1}, \vec{R}; E_\alpha), \end{aligned} \tag{10}$$

where again E_α stands for $E_\alpha^{(n+1)}$. Here I introduce the nth Green's function. Similarly to the function $S^{(n)}$ above, it can be written in the form

$$G^{(n)}(\vec{R}, \vec{R}'; E) = \sum_{\alpha=1}^{Q^{(n)}} \frac{f_\alpha^{(n)*}(\vec{R}) f_\alpha^{(n)}(\vec{R}')}{E_\alpha^{(n)} - E} + \pi i \rho(E) P^{(n)}(\vec{R}, \vec{R}'; E) + \lim_{\gamma \to 0} \int d\epsilon\, \rho(\epsilon) \frac{P^{(n)}(\vec{R}, \vec{R}'; \epsilon)}{(\epsilon - E)^2 + \gamma^2}, \tag{11}$$

where $P^{(n)}(\vec{R}, \vec{R}'; E) = \langle N f_{\vec{k}}^{(n)*}(\vec{R}) f_{\vec{k}}^{(n)}(\vec{R}')\rangle$, the average being over the energy shell $\epsilon_{\vec{k}} = E$. The limit as $\gamma \to 0$ is to yield the principal-part value of the integral; however, a small but finite γ is useful in numerical work. I note that $S^{(n)}(E) = G^{(n)}(\vec{R}_{n+1}, \vec{R}_{n+1}; E)$ is a special case of (11).

The remaining eigenstates are scattering states, with $\vec{k}$ labeling the Bloch state into which they revert when all V_j are allowed to vanish. As the energies $\epsilon_{\vec{k}}^{(n+1)}$ interlace the previous $\epsilon_{\vec{k}}^{(n)}$, all must

differ from the unperturbed Bloch energies by amounts $O(N_I/N) \to 0$. Thus, in all but the most delicate subtraction processes we may continue to use the unperturbed $\epsilon_{\vec{k}}$ and $\rho(\epsilon)$ for the continuum states. Their amplitudes are readily found to be

$$f_{\vec{k}}^{(n+1)}(\vec{R}) = f_{\vec{k}}^{(n)}(\vec{R}) + \frac{V_{n+1} f_{\vec{k}}^{(n)}(\vec{R}_{n+1}) G^{(n)}(\vec{R}_{n+1}, \vec{R}; \epsilon_{\vec{k}})}{1 + V_{n+1} S^{(n)}(\epsilon_{\vec{k}})}. \tag{12}$$

Starting at $n=0$ with $f_{\vec{k}}^{(0)}(\vec{R}) = N^{-1/2} \exp i\vec{k}\cdot\vec{R}$ we iterate (6)–(12) a total of N_I times to obtain the eigenfunctions of the total Hamiltonian $H^{(N_I)} = H_0 + V^{(N_I)}$. This will in general have to be done numerically, and an internal check on the accuracy could be obtained by ordering the defects in different sequences $1, \ldots, N_I$ and checking whether the final answers agree to the desired accuracy.

The length of such calculations is proportional to the number of numerical operations required. $G^{(n)}(\vec{R}, \vec{R}'; E)$ as given in (11) needs only be known at the points $\vec{R} = \vec{R}_{n+1}$ and $\vec{R}' = \vec{R}_{n+1}$ and $\vec{R}_{n+2}$. The final $G^{(N_I)}(\vec{R}, \vec{R}'; E)$ will be required at all lattice points $\vec{R}, \vec{R}'$ within a finite neighborhood of the defects, and over the entire range of energies. Thus, the calculation will take $O(N_I)$ steps—conceivably, a large multiple of N_I plus a large constant. This must be compared to the conventional method, in which the equations

$$\sum_{j=1}^{N_I} \{\delta_{\vec{R}_i, \vec{R}_j} + V(\vec{R}_j) G^{(0)}(\vec{R}_i, \vec{R}_j; E)\} f_{\vec{k}}(\vec{R}_j) = f_{\vec{k}}^{(0)}(\vec{R}_i) \tag{13}$$

are to be solved for $i = 1, 2, \ldots, N_I$ yielding

$$f_{\vec{k}}(\vec{R}) = f_{\vec{k}}^{(0)}(\vec{R}) - \sum_{i=1}^{N_I} G^{(0)}(\vec{R}, \vec{R}_i; E) V(\vec{R}_i) f_{\vec{k}}(\vec{R}_i) \tag{14}$$

at all lattice sites $\vec{R}$. Aside from the time required to compute $G^{(0)}$ at all $\vec{R}, \vec{R}'$, comparable to the calculation of $G^{(N_I)}$ required in the last step of my method, the solution of (13) requires matrix inversion which typically takes $O(N_I^3)$ steps. It is clear that for large values of N_I, perhaps $O(100)$ or so, my new method becomes quite advantageous.

We now turn briefly to the special but interesting case of weak coupling, for which the formulas take on a deceptively simple appearance. It must be assumed that the N_I potentials, while of arbitrary sign, strength, and location, are nonetheless all sufficiently weak and distant from each other that no bound states exist,[5] i.e., all $Q^{(n)} = 0$. Then, all amplitudes take the scattering form (12), all energies lie in the unperturbed continuum, and we can readily express the exact amplitudes in the following canonical form:

$$f_{\vec{k}}^{(n)}(\vec{R}) = N^{-1/2} \{e^{i\vec{k}\cdot\vec{R}} + \textstyle\sum_{\vec{k}'} M_{\vec{k},\vec{k}'}^{(n)} e^{i\vec{k}'\cdot\vec{R}}\}, \tag{15}$$

where $M^{(n)}$ is determined by the forward recursion relations

$$M_{\vec{k},\vec{k}'}^{(n+1)} = M_{\vec{k},\vec{k}'}^{(n)} + L_{\vec{k},\vec{k}'}^{(n)} + \textstyle\sum_{\vec{k}''} L_{\vec{k},\vec{k}''}^{(n)} M_{\vec{k}'',\vec{k}'}^{(n)}, \tag{16}$$

with

$$L_{\vec{k},\vec{k}'}^{(n)} = \frac{f_{\vec{k}'}^{(n)*}(\vec{R}_{n+1}) f_{\vec{k}}^{(n)}(\vec{R}_{n+1}) V_{n+1}}{(\epsilon_{\vec{k}} - \epsilon_{\vec{k}'})[1 + V_{n+1} S^{(n)}(\epsilon_{\vec{k}})]} \tag{17}$$

and the initial condition $M^{(0)} \equiv 0$. Note the extreme nonlinearities: Each $M^{(n)}$ depends on the preceding $L^{(m)}$ not only explicitly through (17) but also through the dependence of the $S^{(m)}$ on $f_{\vec{k}}^{(m)}$, which in turn depend on $M^{(m)}$ through (15), the latter given in terms of $L^{(m)}$ in (16). Nevertheless, these expressions may be useful in recovering familiar approximation schemes; for example, if we retain only terms linear in the potentials, we immediately obtain all the formulas of first-order perturbation theory.

Finally, for hard-core potentials $V_j = \infty$ (suitable if the defects are vacancies), the bound states are projected up out of the band and the formulas (15) and (16) apply here also, with (17) replaced by its $V_{n+1} = \infty$ limit. The interesting parameter here is the geometry of the N_I defects, that is, the manner in which the clustering of the vacancies affects the scattering states.

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[1]M. Goldberger and K. Watson, *Collision Theory* (Wiley, New York, 1964); T.-Y. Wu and T. Ohmura, *Quantum*

Theory of Scattering (Prentice-Hall, Englewood Cliffs, New Jersey, 1962).

[2]W. Harrison, *Solid State Theory* (McGraw-Hill, New York, 1970); G. Weinreich, *Solids, Elementary Theory for Advanced Students* (Wiley, New York, 1965).

[3]G. Koster and J. Slater, Phys. Rev. 95, 1167 (1954), and 96, 1208 (1954); M. Lax, Phys. Rev. 94, 1391 (1954). J. Callaway, J. Math. Phys. (N.Y.) 5, 783 (1964), discussed this model as a special case of the general scattering theory of defects.

[4]Some, or all, can be below or above the band depending on signs, strengths, and proximities of the first n defects. We can thus study the formation of "impurity bands" or "energy tails" due to impurity clustering, as a function of the size of the cluster, by our method. See also B. I. Halperin and M. Lax, Phys. Rev. 148, 722 (1966).

[5]The absence of bound states is tantamount to the condition for perturbation theory on the V_j to be correct. This therefore excludes one or two dimensions, in which the infrared divergence in $S^{(0)}(E)$ guarantees that at least one of the $Q^{(n)} \neq 0$, viz., $Q^{(0)} = 1$, regardless of the sign or strength of V_1. Thus perturbation expansions would appear to be valid only in three or higher dimensions.