M2 ICFP
Theoretical Condensed Matter

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Problem 3 : Scattering and Friedel sum rule

We consider electrons scattering on some impurity described by a potential V. Neglecting electron-electron interactions, the quantum mechanical problem boils down to a one-body problem, with Hamiltonian

$$H = H_0 + V \tag{1}$$

with H_0 the Hamiltonian of an electron without impurity (later we will focus on $H_0 = \frac{\mathbf{p}^2}{2m}$). The objective is to derive the Friedel sum rule, *i.e.* to compute ΔN, the variation of the number of electrons due to the impurity.

Local density of states

For now we consider a generic one-body Hamiltonian $H = \sum_n \epsilon_n |\varphi_n\rangle\langle\varphi_n|$, for which the density of states (DOS) is defined as follow : $\rho(\epsilon)\, d\epsilon$ is the number of one-particle states with an energy between ϵ and $\epsilon + d\epsilon$. Formally this is

$$\rho(\epsilon) = \sum_n \delta(\epsilon - \epsilon_n) \tag{2}$$

A natural definition for the local density of states (LDOS) in real space is

$$\rho(\mathbf{r}, \epsilon) = \sum_n |\langle \mathbf{r}|\varphi_n\rangle|^2 \delta(\epsilon - \epsilon_n) \tag{3}$$

The interpretation of the LDOS is a space-resolved version of the DOS. In the case where all the eigenstates with energy between ϵ and $\epsilon + d\epsilon$ are occupied (*i.e.* as long as $\epsilon < \epsilon_F$), then $\rho(\mathbf{r}, \epsilon)\, d\epsilon\, d^3\mathbf{r}$ is simply the average number of electrons at position $\mathbf{r}$ (up to $d^3\mathbf{r}$) and energy ϵ (up to $d\epsilon$).

1. Show that the formula (3) is equivalent to

$$\rho(\mathbf{r}, \epsilon) = -\frac{1}{\pi} \operatorname{Im} \langle \mathbf{r}|G^+(\epsilon)|\mathbf{r}\rangle \tag{4}$$

   where G^+ is the retarded Green's function of H. While equation (3) is a rather natural way to define the LDOS for non-interacting particles, it is restricted to non-interacting systems. By extension the notion of LDOS is extended to interacting systems using (4).

2. Consider a system of non-interacting fermions at Fermi energy ϵ_F and temperature T. How can the electronic density $\rho(\mathbf{r})$ be recovered from the LDOS ? And the number of fermions N ?

3. From now on we consider an Hamiltonian of the form $H = H_0 + V$. We denote by $G^{\pm}(\omega)$ the retarded and advanced Green's functions of the full Hamiltonian H, and by $G_0^{\pm}(\omega)$ the one of the free Hamiltonian H_0. Let $\Delta\rho(\epsilon)$ be the variation of the DOS due to the impurity. Show that

$$\Delta\rho(\epsilon) = -\frac{1}{\pi}\,\mathrm{Im}\,\mathrm{Tr}\,\left(G^+(\epsilon) - G_0^+(\epsilon)\right) \tag{5}$$

4. Show that the electron retarded Green's function G^+ is given by

$$G^+(\epsilon) = G_0^+(\epsilon) + G_0^+(\epsilon)T^+(\epsilon)G_0^+(\epsilon) \tag{6}$$

where G_0^+ is the retarded Green's function of electrons without the impurity and $T^+(\epsilon) = V(I - G_0^+(\epsilon)V)^{-1}$ is the T (transfer) matrix.

5. Using $\frac{d}{d\epsilon}\mathrm{Tr}\log A(\epsilon) = \mathrm{Tr}\left(A^{-1}(\epsilon)\frac{dA}{d\epsilon}\right)$ show that

$$\Delta\rho(\epsilon) = \frac{1}{\pi}\frac{d}{d\epsilon}\Im\log\det(\mathbb{1} - G_0^+(\epsilon)V)^{-1} \tag{7}$$

6. Deduce from the previous result that

$$\boxed{\Delta\rho(\epsilon) = -\frac{i}{2\pi}\frac{d}{d\epsilon}\log\det\left(\mathbb{1} - i2\pi\delta(\epsilon - H_0)T^+(\epsilon)\right)} \tag{8}$$

Scattering

We look at the case of (non relativistic) free electrons scattering on some impurity described by a potential V, so

$$H = H_0 + V, \qquad H_0 = \frac{\mathbf{p}^2}{2m} \tag{9}$$

The Lippmann-Schwinger equation

We are only concerned with scattering states, that is we will not consider potential bound states around the impurity. As long as the potential has a fast enough falloff at large distances, we can prepare a wavepacket in the far past (or in the far future) in a free state (very far from the impurity).

While the scattering problem should in principle be addressed with localized wave-packets, it is more convenient to look at stationary states (*i.e.* eigenstates of H) while preserving this notion of in and out states. The proper definition of these *scattering states* turns out to tricky mathematically. Heuristically we would like to have a dressed state $|\Psi_{\mathbf{p}}^{\pm}\rangle$ (with energy $\epsilon_{\mathbf{p}} = \frac{\mathbf{p}^2}{2m}$) that looks like the standing wave $|\mathbf{p}\rangle$ in the distant past (future), namely

$$\lim_{t\to\mp\infty}\left(e^{-iHt}|\Psi_{\mathbf{p}}^{\pm}\rangle - e^{-iH_0t}|\mathbf{p}\rangle\right) = 0$$

for some appropriate sense of limit. Naively we would like to define operators

$$\Omega^{\pm} \stackrel{?}{=} \lim_{t\to\mp\infty} e^{iHt}e^{-iH_0t}$$

Provided the potential $V(\mathbf{r})$ has a $|\mathbf{r}|^{-1-\epsilon}$ falloff at large distances, this limit can be shown to converge when acting on wave-packets. However when acting on a plane wave $\langle \mathbf{r}|\mathbf{p}\rangle = e^{i\mathbf{r}\cdot\mathbf{p}}$ taking this limit is a more subtle matter. The physicist's answer[1] is to regularize this limit with a damping factor $e^{-\eta|t|}$, before sending $\eta \to 0^+$. In order to motivate this regularization, we start off with the following result :

7. *Abelian limit.* Let $g(t)$ be a function such that $g'(t)$ is bounded and $\lim_{t\to\infty} g(t)$ exists. Check that

$$\lim_{t\to\infty} g(t) = \lim_{\eta\to 0} \int_0^\infty ds\, \eta e^{-\eta s} g(s) \tag{10}$$

This leads us to define the Møller wave operators $\Omega^\pm$ and scattering state $|\Psi^\pm_{\mathbf{p}}\rangle$ as

$$|\Psi^\pm_{\mathbf{p}}\rangle = \Omega^\pm |\mathbf{p}\rangle, \qquad \Omega^\pm = \mp \lim_{\eta\to 0^+} \int_0^{\mp\infty} dt\, \eta e^{\pm\eta t} e^{iHt} e^{-iH_0 t} \tag{11}$$

The Møller wave operators are *isometries*[2], in the sense that $(\Omega^\pm)^\dagger\, \Omega^\pm = \mathbb{1}$.

8. With this definition, check that $H\Omega^\pm = \Omega^\pm H_0$. This ensures that the scattering states $|\Psi^\pm_{\mathbf{p}}\rangle$ have the same energy as $|\mathbf{p}\rangle$, as expected for elastic scattering.

9. Show that the in and out states $|\Psi^\pm_{\mathbf{p}}\rangle$ obey

$$|\Psi^\pm_{\mathbf{p}}\rangle = \lim_{\eta\to 0^+} \frac{\pm i\eta}{\epsilon_{\mathbf{p}} \pm i\eta - H} |\mathbf{p}\rangle$$

and derive the **Lippmann-Schwinger equation**:

$$\boxed{|\Psi^\pm_{\mathbf{p}}\rangle = |\mathbf{p}\rangle + G_0^\pm\left(\epsilon_{\mathbf{p}}\right) V |\Psi^\pm_{\mathbf{p}}\rangle} \tag{12}$$

10. Show that the Lippmann-Schwinger equation is equivalent to:

$$|\Psi^\pm_{\mathbf{p}}\rangle = (\mathbb{1} + G^\pm\left(\epsilon_{\mathbf{p}}\right) V)|\mathbf{p}\rangle. \tag{13}$$

11. Show that the Green's functions in real space $\langle \mathbf{r}|G_0^\pm(\epsilon)|\mathbf{r}'\rangle$ (a.k.a. propagator) for a free electron with $H_0 = \frac{\mathbf{p}^2}{2m}$ is given by

$$\langle \mathbf{r}|G_0^\pm(\epsilon)|\mathbf{r}'\rangle = -\frac{m}{2\pi}\frac{e^{\pm ik|\mathbf{r}-\mathbf{r}'|}}{|\mathbf{r}-\mathbf{r}'|}, \qquad \text{where} \qquad k = \sqrt{2m\epsilon} \tag{14}$$

[1] For the more mathematically inclined, a more rigorous discussion can be found in the introduction of *Methods of modern mathematical physics Vol. 3 : Scattering theory* by M. Reed and B. Simon.

[2] However the Møller wave operators are not unitary ! The image of $\Omega^\pm$ is the called *absolutely continuous subspace* of H, which is the subspace perpendicular to all bound-states of H.). This means that we dot not have $\Omega^\pm\,(\Omega^\pm)^\dagger = 1$, because the adjoint operator $(\Omega^\pm)^\dagger$ is only defined on this subspace.

12. Assuming that impurity potential is short ranged, argue that the scattering states $|\Psi^{\pm}_{\mathbf{p}}\rangle$ have the following asymptotic behavior far from the impurity

$$\langle \mathbf{r}|\Psi^{\pm}_{\mathbf{p}}\rangle \sim e^{i\mathbf{r}\cdot\mathbf{p}} + f^{\pm}(\mathbf{k},\mathbf{p})\frac{e^{\pm ipr}}{r}, \qquad \mathbf{k} = p\hat{\mathbf{r}}, \qquad \hat{\mathbf{r}} = \frac{\mathbf{r}}{r} \tag{16}$$

where $f^{\pm}(\mathbf{k},\mathbf{p})$ is called the diffusion amplitude. Show that

$$f^{\pm}(\mathbf{k},\mathbf{p}) = -\frac{m}{2\pi}\langle \pm\mathbf{k}|V|\Psi^{\pm}_{\mathbf{p}}\rangle = -\frac{m}{2\pi}\langle \pm\mathbf{k}|T^{\pm}(\epsilon_{\mathbf{p}})|\mathbf{p}\rangle \tag{17}$$

In view of this asymptotic behavior, what is the natural interpretation of the Lippmann-Schwinger equation ?

S-matrix

The S-matrix gives the relation between in and out states, and is defined as

$$\langle \mathbf{p}|S|\mathbf{q}\rangle = \langle \Psi^{-}_{\mathbf{p}}|\Psi^{+}_{\mathbf{q}}\rangle \tag{18}$$

13. Show that the S matrix and the T matrix are related as follow

$$\langle \mathbf{p}|S|\mathbf{p}'\rangle = (2\pi)^3\,\delta^{(3)}(\mathbf{p}-\mathbf{p}') - 2\pi i\delta(\epsilon_{\mathbf{p}} - \epsilon_{\mathbf{p}'})\langle \mathbf{p}|T^{+}(\epsilon_{\mathbf{p}})|\mathbf{p}'\rangle \tag{19}$$

This means that S is completely determined by the values of $\langle \mathbf{p}|T^{+}(\epsilon_{\mathbf{p}})|\mathbf{p}'\rangle$ for $\epsilon_{\mathbf{p}} = \epsilon_{\mathbf{p}'}$, which is referred to as the "on-shell" T-matrix.

14. The S-matrix commutes with H_0, and therefore is block diagonal w.r.t. to the energy ϵ. Let $S(\epsilon)$ be the restriction of S to the subspace $H_0 = \epsilon$. Starting from (8), show that

$$\boxed{\Delta\rho(\epsilon) = -\frac{i}{2\pi}\frac{d}{d\epsilon}\log\det S(\epsilon)} \tag{20}$$

Central potential : phase shifts

In this section we consider the spacial case of a spherically symmetric impurity.

The rotational symmetry of the impurity implies that V commutes with $\mathbf{L}$: we have conservation of angular momentum. While the proper physical setup is that of an incident plane wave, the conservation of angular momentum tells us that the scattering problem is going to look much simpler for incident states that are eigenstates of $\mathbf{L}^2$ and L_z (and H_0). Let's label by $|p,l,m\rangle$ the state obeying

$$H_0|p,l,m\rangle = \frac{p^2}{2m}|p,l,m\rangle, \qquad \mathbf{L}^2|p,l,m\rangle = l(l+1)|p,l,m\rangle, \qquad L_z|p,l,m\rangle = m|p,l,m\rangle$$

The states $|p,l,m\rangle$ are called spherical waves, see Appendix.

15. Argue that the S-matrix is diagonal in this basis, and that the corresponding eigenvalues only depend on p and l. Namely

$$\langle p',l',m'|S|p,l,m\rangle = \frac{\pi}{2p^2}\delta(p'-p)\delta_{l',l}\delta_{m',m}\,S_l(p) \tag{21}$$

16. Show that

$$S_l(p) = 1 - 4ip\,m\,T_l(p)$$

with $T_l(p) = \langle p, l, m|T(\epsilon_p)|p, l, m\rangle$.

The states $|p, l, m\rangle$ are spherical waves as can be seen from the asymptotic behavior for large r

$$j_l(pr) \sim \frac{1}{pr}\sin\left(pr - \frac{1}{2}l\pi\right)$$

This solution is obtained by separation of variables $\Psi(r, \theta, \phi) = R_l(r)Y_l^m(\theta, \phi)$ and then solving the second order differential equation for the radial part $R_l(r)$

$$-\frac{1}{r^2}\partial_r(r^2\partial_r R_l(r)) + \frac{l(l+1)}{r^2}R_l(r) = p^2 R_l(r)$$

while imposing that the solution be regular as $r \to 0$. In the presence of the potential $V(r)$, this differential equation becomes

$$-\frac{1}{r^2}\partial_r(r^2\partial_r R_l(r)) + \left(2mV(r) + \frac{l(l+1)}{r^2}\right)R_l(r) = p^2 R_l(r)$$

Under some relatively mild assumptions[3] one can show that the solution that is regular at the origin behaves for large r as

$$R_l(r) \sim \frac{1}{pr}\sin\left(pr - \frac{1}{2}l\pi + \delta_l(p)\right) \tag{22}$$

The only effect of of the scattering potential at large r is to add a **phase shift** $\delta_l(p)$ to the out-going wave. A priori these phase shifts are only defined mod π, but this ambiguity can be lifted by demanding that the functions $\delta_l(p)$ are continuous functions of p and that $\delta_l(\infty) = 0$.

17. Argue that near the origin the partial wave $R_l(r)$ behaves as $R_l(r) \sim r^l$. This leads to the so-called **threshold behavior** : for most potentials, there is a critical value of the energy below which the s-wave part of the incident wave dominates the scattering amplitude.

18. Show that the eigenvalues of the S matrix are $e^{2i\delta_l(p)}$ (you can try to calculate the large r behaviour of $|p, l, m\rangle_{\text{in}}$).

19. Show that

$$\boxed{\Delta\rho(\epsilon) = \frac{d}{d\epsilon}\frac{1}{\pi}\sum_{l=0}^{\infty}(2l+1)\delta_l(\epsilon)} \tag{23}$$

[3]For instance if the potential $V(r)$ vanishes faster than r^{-1} at large distances, and is less singular than r^{-2} at the origin, Thm XI.53 in *Methods of modern mathematical physics Vol. 3 : Scattering theory* by M. Reed and B. Simon. This result is not very surprising since for large r the differential equation boils down to $\partial_r(r^2\partial_r R_l(r)) = -r^2p^2R_l(r)$, whose solutions are spherical waves $e^{\pm ipr}/r$. However this naive reasoning can be misleading, and turns out not to be correct in for Coulomb interaction where $V(r) \sim 1/r$, in which case the correct asymptotic behavior is of the form $r^\alpha e^{\pm ipr}/r$, where α is proportional to the interaction strength.

20. Derive the Friedel sum rule :

$$\Delta N(\epsilon_F) = N_B + \frac{1}{\pi}\sum_{l=0}^{\infty}(2l+1)\left(\delta_l(\epsilon_F) - \delta_l(0)\right) \tag{24}$$

relating the phase shifts to the variation of the electron number $\Delta N(epsilon_F)$ caused by the presence of the impurity at Fermi energy ϵ_F. N_B is the number of bound states of the Hamiltonian $H_0 + V$.

A very interesting and peculiar result of scattering theory is the the number of bound states and the phase shifts are not independent. Levinson's theorem relates the number of bound states $N_{B,l}$ of angular momentum l to the phase shift at zero energy $\delta_l(0)$, namely

$$N_{B,l} = (2l+1)\frac{\delta_l(0)}{\pi} \tag{25}$$

Using this result Friedel sum rule can be written as

$$\boxed{\Delta N(\epsilon_F) = \frac{1}{\pi}\sum_{l=0}^{\infty}(2l+1)\delta_l(\epsilon_F)} \tag{26}$$

1 Friedel oscillations

21. Show that the variation of electron density caused by the impurity at Fermi energy ϵ_F is

$$\Delta\rho(\mathbf{r}) = \sum_{\alpha=1}^{N_B}|\langle\mathbf{r}|\phi_\alpha\rangle|^2 + \sum_{l,m}\int_0^{k_F}\frac{2p^2dp}{\pi}\,|\langle\mathbf{r}|p,l,m\rangle^+|^2 - |\langle\mathbf{r}|p,l,m\rangle|^2 \tag{27}$$

where $|\phi_\alpha\rangle$ are the bound states of H.

22. Using $\sum_{m=-l}^{l}|Y_l^m(\hat{\mathbf{r}})| = (2l+1)/4\pi$, argue that for large $\mathbf{r}$, we have

$$\Delta\rho(\mathbf{r}) \sim \frac{1}{r^2}\sum_l\frac{(2l+1)}{2\pi^2}\int_0^{k_F}dp\left[\sin^2\left(pr - \frac{1}{2}l\pi + \delta_l(p)\right) - \sin^2\left(pr - \frac{1}{2}l\pi\right)\right] \tag{28}$$

23. Using an integration by part, show that the leading asymptotic contribution to this integral gives:

$$\Delta\rho(r) \sim -\frac{1}{4\pi^2r^3}\sum_l(2l+1)(-1)^l\cos(2k_Fr + \delta_l(k_F))\sin\delta_l(k_F) \tag{29}$$

Appendix : spherical waves

While the plane waves are the eigenstates of $H_0 = \frac{\mathbf{p}^2}{2m}$, and the momentum $\mathbf{P}$, the spherical waves are eigenstates of $\mathbf{L}^2$ and L_z (and H_0). Let $|p,l,m\rangle$ be the spherical wave defined as

$$H_0|p,l,m\rangle = \frac{p^2}{2m}|p,l,m\rangle, \qquad \mathbf{L}^2|p,l,m\rangle = l(l+1)|p,l,m\rangle, \qquad L_z|p,l,m\rangle = m|p,l,m\rangle$$

Its wave-functions in spherical coordinates is given by

$$\langle r,\theta,\phi|p,l,m\rangle = j_l(pr)Y_l^m(\theta,\phi)$$

where $Y_l^m(\theta,\phi)$ are the spherical harmonics, and $j_l(pr)$ is the spherical Bessel function of the first kind. The normalization has been chosen such that

$$\langle p',l',m'|p,l,m\rangle = \frac{\pi}{2p^2}\delta(p'-p)\delta_{l',l}\delta_{m',m} \qquad \text{and} \qquad 1 = \int_0^\infty \frac{2p^2dp}{\pi}\sum_{l,m}|p,l,m\rangle\langle p,l,m|$$

Of course the plane-wave $|\mathbf{p}\rangle$ can be decomposed as a superposition of these spherical waves. One finds

$$|\mathbf{p}\rangle = 4\pi\sum_{l,m} i^l Y_l^{m*}(\hat{\mathbf{p}})|p,l,m\rangle \tag{30}$$

or equivalently

$$e^{i\mathbf{p}\cdot\mathbf{r}} = 4\pi\sum_{l=0}^{\infty}\sum_{m=-l}^{l} i^l j_l(pr)Y_l^m(\hat{\mathbf{r}})Y_l^{m*}(\hat{\mathbf{p}}) \tag{31}$$

It is a good exercise to check all these relations, using the following identities

$$\int_0^\infty r^2dr\, j_l(p'r)j_l(pr) = \frac{\pi}{2p^2}\delta(p-p'), \qquad\qquad \int d^2\hat{\mathbf{r}}\, Y_{l'}^{m'*}(\hat{\mathbf{r}})Y_l^m(\hat{\mathbf{r}}) = \delta_{l,l'}\delta_{m,m'}$$