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PERTURBATION THEORY OF THE SELF-CONSISTENT FIELD

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A. K. Rajagopal

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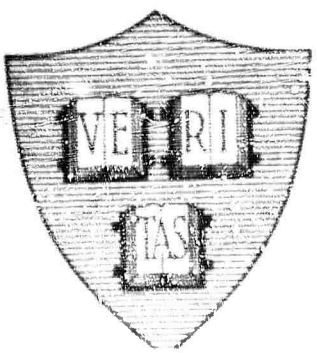

DIVISION OF ENGINEERING AND APPLIED PHYSICS
HARVARD UNIVERSITY • CAMBRIDGE, MASSACHUSETTS

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Division of Engineering and Applied Physics

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ABSTRACT

A perturbation theory of the self-consistent field is here developed using a Green's function method after the manner of Peng. It is shown that a self-consistent perturbation theory yields the same answers as the conventional random phase approximation. The equivalence of the perturbation approach to spin waves in metals developed by Herring and the random phase approximation for the same problem is seen to be an example of this. The effect of the weak periodic field on a Hartree-Fock electron system is here explicitly done both by the perturbation approach and the the random phase approximation with the Green's function approach. The Green's function approach is finally generalized so as to include, in principle, correlations beyond the Hartree-Fock.

PERTURBATION THEORY OF THE SELF-CONSISTENT FIELD

by

A. K. Rajagopal*

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INTRODUCTION

About twenty years ago, Peng wrote a paper [1] with the above title, developing a straightforward perturbation theory of the Hartree-Fock (HF) self-consistent field equations when there is a small perturbing term in the Hamiltonian. This method was used a decade later by Herring [2] in demonstrating the existence of spin waves in metals. Recently, this problem has been reexamined by many authors in the random phase approximations (RPA). In particular, the present author noted [3] (where references to other work could be found) the close relationship between Herring's work and the RPA results he obtained by a Green's function approach. But at the time of writing about it, we were not aware of an explicit relationship between the two apparently different approaches to such problems, although the equivalence of the two methods was surmised. In this report, a proof of this equivalence is explicitly constructed, in response to repeated demands for one by Professor Brooks earlier and more recently by Dr. Herring. It might also be of interest to mention here that the work of Thouless [4] on RPA is closely related to that of Peng [1], even though Thouless uses a variational method

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and Peng, a perturbation approach. Slater [5], in his Quantum Theory of Atomic Structure, Volume I, has a demonstration of the following simple theorem: The equations obtained in a variational principle involving a certain basis set of functions are the same as those involving a perturbation approach where the same basis set is used as the zero-order functions. The present report demonstrates this even when one has nonlocal self-consistent field equations.

In most many-electron calculations, one deals with a uniform electron gas with a uniform compensating positive background. We first treat, by the present techniques, the effect of a weak periodic positive background on a HF electron gas. (Professor Brooks informed the author that he gave this problem in one of his advanced courses on quantum theory of solids ten years ago at Harvard University!) This is essentially the nearly free-electron problem when we have HF correlations. See Anderson [6] for a discussion of the same in the absence of HF correlations. We do this problem first by the Peng method and then by the Green's function approach. Finally, we generalize this Green's function approach formally when the electron interactions are taken into account beyond the HF approximation. This problem was suggested to the author by Professor Ehrenreich. The results are quite similar to the recent work of Tanaka [7], who uses a diagrammatic approach to this problem.

PENG'S PERTURBATION EQUATIONS AND RANDOM PHASE APPROXIMATION

We first collect Peng's [1] results and compare them with the RPA of Thouless [4]. Then we go on to develop a Green's function reformulation of the same type of perturbation theory in the HF approximation. We then explicitly demonstrate the equivalence of our equations obtained here with those obtained earlier [3] for the case of spin waves in an electron gas. In the next section, we examine the effect of a weak periodic field on a many-electron system.

Peng proceeds as follows. The HF equations for an n-electron system are

$$(T + V + G - E_\gamma)\,\phi_\gamma = 0 \quad (\gamma = 1,\ 2,\ \ldots\ n) \tag{1}$$

T is the one-electron operator containing the kinetic and potential energies. V is the one-electron external potential to be treated in perturbation theory. (Peng used a more general set of perturbing terms; we have simplified it here for the present purposes.) And G is the HF operator defined by

$$G\,\phi_\gamma = \sum_{\lambda=1}^{n} [(\phi_\lambda,\ v\,\phi_\lambda)\,\phi_\gamma - (\phi_\lambda,\ v\,\phi_\gamma)\,\phi_\lambda] \tag{2}$$

the first being the Coulomb term, and the second the exchange term, and

$$(\phi_\lambda,\ v\,\phi_\gamma) \equiv \sum_{s'} \int dr'\ \phi_\lambda^*(r's')\, v(rs;r's')\,\phi_\gamma(r's') \tag{3}$$

where v is the two-particle interaction potential which is self-adjoint and symmetric. s is the spin variable. In most cases, $v = e^2/|\vec{r} - \vec{r}'|$. The energy parameters E_γ are the HF one-electron energies. Let the unperturbed HF problem be assumed to have been solved:

$$(T + G - E_\beta^{(0)})\,\phi_\beta^{(0)} = 0 \tag{4}$$

where

$$G\phi_\beta^{(0)} = \sum_{\lambda=1}^{n} [(\phi_\lambda^{(0)}, v\,\phi_\lambda^{(0)})\,\phi_\beta^{(0)} - (\phi_\lambda^{(0)}, v\,\phi_\beta^{(0)})\,\phi_\lambda^{(0)}]\,. \tag{5}$$

Note that since the operator G is self adjoint and linear, the set $\left\{\phi_\beta^{(0)}\right\}$ is orthonormal. One may therefore write

$$\phi_\gamma = \sum_\beta \phi_\beta^{(0)} \mathcal{U}_{\beta\gamma}\,. \tag{6}$$

Writing

$$\left.\begin{aligned} &(\phi_\alpha^{(0)},\ T\phi_\beta^{(0)}) = T_{\alpha\beta}\ ;\quad (\phi_\alpha^{(0)},\ V\phi_\beta^{(0)}) = V_{\alpha\beta} \\ &\text{and} \\ &(\phi_\alpha^{(0)},\ (\phi_\mu^{(0)}\ v\,\phi_\nu^{(0)})\,\phi_\beta^{(0)}) = v_{\alpha\mu\nu\beta} \end{aligned}\right\} \tag{7}$$

Eq. (1) may be written as

$$\sum_\beta \left[T_{\alpha\beta} + V_{\alpha\beta} + \sum_{\lambda=1}^{n} \sum_{\mu\nu} \mathcal{U}_{\mu\lambda}^{*} (v_{\alpha\mu\,\nu\beta} - v_{\alpha\mu\beta\nu}) \mathcal{U}_{\nu\lambda} - E_\gamma \delta_{\alpha\beta}\right] \mathcal{U}_{\beta\gamma} = 0 \tag{8}$$

Let us denote $V_{\alpha\beta} = V_{\alpha\beta}^{(1)}$, being of first order in perturbation. (9)

Then write

$$\left.\begin{aligned} \mathcal{U}_{\beta\gamma} &= \delta_{\beta\gamma} + \mathcal{U}_{\beta\gamma}^{(1)} + \mathcal{U}_{\beta\gamma}^{(2)} + \dots \\ E_\gamma &= E_\gamma^{(0)} + E_\gamma^{(1)} + E_\gamma^{(2)} + \dots \end{aligned}\right\} \tag{10}$$

One then has

$$E_a^{(0)} = T_{aa} + \sum_{\lambda=1}^{n} (v_{a\lambda\lambda a} - v_{a\lambda a\lambda})$$

and

$$T_{a\gamma} + \sum_{\lambda=1}^{n} (v_{a\lambda\lambda\gamma} - v_{a\lambda\gamma\lambda}) = 0 \quad (a \neq \gamma) \qquad (11a)$$

$$E_a^{(1)} = V_{aa}^{(1)} + \sum_{\lambda=1}^{n} \sum_{\mu} [(v_{a\lambda\mu a} - v_{a\lambda a\mu}) \mathcal{U}_{\mu\lambda}^{(1)} + (v_{a\mu\lambda a} - v_{a\mu a\lambda}) \mathcal{U}_{\mu\lambda}^{(1)*}] \qquad (11b)$$

and

$$(E_a^{(0)} - E_\gamma^{(0)}) \mathcal{U}_{a\gamma}^{(1)} + \sum_{\lambda=1}^{n} \sum_{\mu} [(v_{a\lambda\mu\gamma} - v_{a\lambda\gamma\mu}) \mathcal{U}_{\mu\lambda}^{(1)} + (v_{a\mu\lambda\gamma} - v_{a\mu\gamma\lambda}) \mathcal{U}_{\mu\lambda}^{(1)*}]$$

$$= - V_{a\gamma}^{(1)} \qquad (a \neq \gamma)$$

$$E_a^{(2)} = \sum_{\lambda=1}^{n} \sum_{\mu} [(v_{a\lambda\mu a} - v_{a\lambda a\mu}) \mathcal{U}_{\mu\lambda}^{(2)} + (v_{a\mu\lambda a} - v_{a\mu a\lambda}) \mathcal{U}_{\mu\lambda}^{(2)*}] +$$

$$+ \sum_{\lambda=1}^{n} \sum_{\mu\nu} (v_{a\mu\nu a} - v_{a\mu a\nu}) \mathcal{U}_{\mu\lambda}^{(1)*} \mathcal{U}_{\nu\lambda}^{(1)}$$

and

$$(E_a^{(0)} - E_\gamma^{(0)}) \mathcal{U}_{a\gamma}^{(2)} + \sum_{\lambda=1}^{n} \sum_{\mu} [(v_{a\lambda\mu\gamma} - v_{a\lambda\gamma\mu}) \mathcal{U}_{\mu\lambda}^{(2)} +$$

$$(v_{a\mu\lambda\gamma} - v_{a\mu\gamma\lambda}) \mathcal{U}_{\mu\lambda}^{(2)*}] =$$

$$= - (E_a^{(1)} - E_\gamma^{(1)}) \mathcal{U}_{a\gamma}^{(1)} - \sum_{\lambda=1}^{n} \sum_{\mu\nu} (v_{a\mu\nu\gamma} - v_{a\mu\gamma\nu}) \mathcal{U}_{\mu\lambda}^{(1)*} \mathcal{U}_{\nu\lambda}^{(1)} \qquad (a \neq \gamma) \qquad (11c)$$

Moreover, the normalization condition gives

$$\left.\begin{aligned} \mathcal{U}^{(1)}_{\gamma k} + \mathcal{U}^{(1)*}_{k\gamma} &= 0 \\ \mathcal{U}^{(2)}_{\gamma k} + \mathcal{U}^{(2)*}_{k\gamma} &= -\sum_{\beta} \mathcal{U}^{(1)*}_{\beta\gamma}\, \mathcal{U}^{(1)}_{\beta k} \quad \text{etc.} \end{aligned}\right\} \tag{11d}$$

Also quite generally one has

$$v^{*}_{\beta\nu\mu\alpha} = v_{\alpha\mu\nu\beta} = v_{\mu\alpha\beta\nu} \quad . \tag{11e}$$

The homogeneous counterpart of the second of the equations (11b) will now be identified with the time-independent RPA equations of Thouless [4] .

Suppose that $q_i^{\dagger}$ creates a particle with wave function ϕ_i . The state with n-electrons occupied, is the Slater determinant

$$|\Phi_o\rangle = \left(\prod_{i=1}^{n} q_i^{\dagger}\right)|0\rangle \tag{12}$$

with $|0\rangle$ representing the vacuum state and such that $\langle\Phi_o|\Phi_o\rangle = 1$. Thouless [4] showed that any n-particle Slater determinant $|\Phi\rangle$ which is not orthogonal to $|\Phi_c\rangle$ can be written in the form

$$|\Phi\rangle = \left[\exp \sum_{i=1}^{n} \sum_{m=n+1}^{\infty} C_{mi}\, q_m^{\dagger} q_i\right]|\Phi_o\rangle \tag{13}$$

where C_{mi} are uniquely determined and conversely that any wave function of this form is an n-particle Slater determinant. Now suppose $|\Phi_o\rangle$ is the HF state. Choose C_{mi} so as to minimize the average energy: $E = \langle\Phi|H|\Phi\rangle/\langle\Phi|\Phi\rangle$. This gives equations of the form (11b) satisfied by $\mathcal{U}^{(1)}_{\alpha\gamma}$, and these are indeed

the RPA equations. Note that to all orders the homogeneous parts of the perturbation equations are the same and of the form of the homogeneous part of (11b). When we generalize this in the Green's function formalism to a time-dependent form, we see the identification with RPA equations even more closely.

Both the Thouless and Peng calculations employ as starting point the complete set of the unperturbed HF solutions. In ordinary Quantum mechanical problems, Slater [5] showed that in such a procedure the perturbation equations and the equations obtained from the variational methods are identical. This is seen to be the case even for the equations of the HF type. Recently, Fukuda [8], without the knowledge of the work of Thouless [4], showed that whenever one has perturbations of the HF states due to any external fields, the new state can be written in the form of a unitary transformation of the type (12). Based on this, he constructs stability conditions for the HF state when one has various external perturbations. This again led him to RPA equations, again in conformity with Peng's calculations.

We will now develop a simple Green's function formulation of the same basic ideas as in Peng's work except writing it in a time-dependent form which has some advantages. Let us consider the HF Green's function equation [3] in the presence of an external perturbing field $V(1)$.

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - U(1) - V(1) + i\int d\bar{3}\, v(1-\bar{3})\, \mathrm{tr}\, G_{HF}(\bar{3}\bar{3}^+) \right] G_{HF}(1\,2) -$$

$$-i\int d\bar{3}\, v(1-\bar{3})\, G_{HF}(1\,\bar{3})\, G_{HF}(\bar{3}\,2) = \delta^{(4)}(1-2) \qquad (14)$$

where $G(12) = \frac{1}{i} \langle T(\psi(1)\psi^{+}(2)) \rangle$ in the usual notation and 1 stands for the space-time point $(r_1 t_1)$. Here $U(1)$ is the one-particle potential in whose presence the problem with $V = 0$ is assumed to be solvable. We have the completeness relation

$$\left.\begin{aligned} \int G_{HF}^{-1}(1\bar{2})\, G_{HF}(\bar{2}1')\, d\bar{2} &= \delta^{(4)}(1-1') \\ \int G_{HF}(1\bar{2})\, G_{HF}^{-1}(\bar{2}1')\, d\bar{2} &= \delta^{(4)}(1-1') \end{aligned}\right\} \tag{15}$$

When $V = 0$, the zero-order HF equation is

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - U(1) + i\int d\bar{3}\, v(1-\bar{3})\, \mathrm{tr}\, G_{HF}^{(0)}(\bar{3}\bar{3}^{+}) \right] G_{HF}^{(0)}(12) - \tag{16}$$

$$-i\int d\bar{3}\, v(1-\bar{3})\, G_{HF}^{(0)}(1\bar{3})\, G_{HF}^{(0)}(\bar{3}2) = \delta^{(4)}(1-2)$$

and

$$\left.\begin{aligned} \int G_{HF}^{(0)\,-1}(1\bar{2})\, G_{HF}^{(0)}(\bar{2}1')\, d\bar{2} &= \delta^{(4)}(1-1') \\ \int G_{HF}^{(0)}(1\bar{2})\, G_{HF}^{(0)\,-1}(\bar{2}1')\, d\bar{2} &= \delta^{(4)}(1-1') \end{aligned}\right\} \tag{17}$$

We now develop a perturbation theory in V. For this purpose we write

$$G_{HF}(12) = G_{HF}^{(0)}(12) + \int \frac{\delta G_{HF}(12)}{\delta V(\bar{3})} V(\bar{3})\, d\bar{3} + \frac{1}{2!}\iint \frac{\delta^2 G_{HF}(12)}{\delta V(\bar{3}_1)\delta V(\bar{3}_2)} V(\bar{3}_1) V(\bar{3}_2) d\bar{3}_1 d\bar{3}_2 + \ldots \tag{18}$$

and

$$G_{HF}^{-1}(12) = G_{HF}^{(0)\,-1}(12) + \int \frac{\delta G_{HF}^{-1}(12)}{\delta V(\bar{3})} V(\bar{3})\, d\bar{3} + \ldots \tag{18'}$$

First let us use the relation (15) to write Eq. (14) in the form

$$G_{HF}^{-1}(12) = \left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - U(1) - V(1) + i\int d\bar{3}\, v(1-\bar{3})\, \mathrm{tr}\, G_{HF}(\bar{3}\bar{3}^+) \right] \delta^{(4)}(1-2) -$$

$$- i\, v(1-2)\, G_{HF}(12) \quad . \tag{19}$$

Then, collecting equations to each order, we have

$$G_{HF}^{(0)\,-1}(12) = \left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - U(1) + i\int d\bar{3}\, v(1-\bar{3})\, \mathrm{tr}\, G_{HF}^{(0)}(\bar{3}\bar{3}^+) \right] \delta^{(4)}(1-2) - iv(1-2) G_{HF}^{(0)}(12) \tag{20a}$$

$$\frac{\delta G_{HF}^{-1}(12)}{\delta V(3)} = -\delta(1-2)\delta(1-3) + i\int d\bar{3}\, v(1-\bar{3})\, \mathrm{tr}\, \frac{\delta G_{HF}(\bar{3}\bar{3}^+)}{\delta V(3)}\, \delta^{(4)}(1-2) -$$

$$- iv(1-2) \left[\frac{\delta G_{HF}(12)}{\delta V(3)} \right] \quad \text{etc.} \tag{20b}$$

Now from (18), (18'), (15) and (17) we have

$$\frac{\delta G_{HF}(12)}{\delta V(3)} = -\int G_{HF}^{(0)}(1\bar{2})\, \frac{\delta G_{HF}^{-1}(\bar{2}\bar{3})}{\delta V(3)}\, G_{HF}^{(0)}(\bar{3}2)\, d\bar{2}\, d\bar{3} \quad . \tag{20c}$$

Substituting this in (20b), we get an equation for $\dfrac{\delta G_{HG}^{-1}(12)}{\delta V(3)}$ to be solved:

$$\frac{\delta G_{HF}^{-1}(12)}{\delta V(3)} = -\delta^{(4)}(1-2)\delta^{(4)}(1-3) - i\int d\bar{2}\, d\bar{3}\, d\bar{4}\, v(1-\bar{2}) \mathrm{tr} \left[G_{HF}^{(0)}(\bar{2}\bar{3}) \frac{\delta G_{HF}^{-1}(\bar{3}\bar{4})}{\delta V(3)} G_{HF}(\bar{4}\bar{2}^+) \right] +$$

$$+ i\, v(1-2) \int d\bar{3}\, d\bar{4}\, G_{HF}^{(0)}(1\bar{3})\, \frac{\delta G_{HF}^{-1}(\bar{3}\bar{4})}{\delta V(3)}\, G_{HF}^{(0)}(\bar{4}2) \quad . \tag{20d}$$

This is just the RPA equation for $\frac{\delta G^{-1}}{\delta V}$ [3]. Note the appearance of $G_{HF}^{(0)}$ in this equation. It is clear that we can generalize the approach when we have a more general $G^{(0)}$. Once (20d) is solved, one puts it back in (18) and looks for the pole in the energy plane in G. We do this explicitly for the case of the weak periodic field in the next section.

At this point we would like to draw attention to the equivalence of Herring's perturbation approach [2] and RPA [3] in the problem of spin waves in metals. Herring calculated, using Peng's equations, the spin wave energy by applying an external static transverse field to second order, it being a time-independent perturbation calculation. We [3] studied the same problem by an approach similar to the one outlined above in the last paragraph using a time-dependent external field, and using RPA. The eigenvalue of this equation was the same as the spin wave energy obtained by Herring. This answers the query raised by Brooks and Herring in private communication. In the next section, we work out an explicit example of this.

WEAK PERIODIC FIELD IN A MANY-ELECTRON SYSTEM

We first study this problem by the Peng approach and then derive the same results and generalizations thereof by the Green's function method. Let the weak periodic field be $V(r)$ such that

$$V(r) = \sum_{K} e^{iK\cdot r} V^{(1)}(K) \quad (K: \text{reciprocal lattice vectors}). \tag{21}$$

In the absence of $V(r)$, the HF equations of a uniform electron gas in a uniform positive background admit of plane waves as solutions. So, we employ these as our basis when V occurs in the problem. Thus,

$$\phi_k(r) = \sum_{K_1} e^{i(k+K_1)\cdot r} \chi(k+K_1) \quad . \tag{22}$$

Then the resulting equation for χ, proceeding as in the last section, is:

$$\frac{|k+K|^2}{2m} \chi(k+K) + \sum_{K_1} V^{(1)}(K_1) \chi(k+K-K_1) +$$

$$+ \sum_{k_1} \sum_{K_1 K_2} [v(K_1-K_2) - v(k_1-k-K-K_2)] \chi^*(k_1+K_1) \chi(k_1+K_2) \chi(k+K+K_1-K_2)$$

$$= E(k) \chi(k+K) \quad . \tag{23}$$

This is the generalized version of the problem of the nearly free electrons [6]. We now write

$$\left.\begin{aligned} \chi(k+K) &= \delta_{K,0} + \chi^{(1)}(k+K) + \chi^{(2)}(k+K) + \ldots \\ E(k) &= E^{(0)}(k) + E^{(1)}(k) + E^{(2)}(k) + \ldots \end{aligned}\right\} . \tag{24}$$

The normalization condition gives:

$$\chi^{(1)}(k) + \chi^{(1)*}(k) = 0 \tag{25a}$$

$$\chi^{(2)}(k) + \chi^{(2)*}(k) = -\sum_{K_1} \chi^{(1)*}(k+K_1) \chi^{(1)}(k+K_1) \text{ etc.} \tag{25b}$$

Then the zero-order equations give the usual HF energy in the absence of V

$$E^{(0)}(k) = \frac{k^2}{2m} + \sum_{k_1} [v(0) - v(k-k_1)] \quad . \tag{26}$$

The first-order equation gives

$$E^{(1)}(k) = V^{(1)}(0) \equiv 0 \text{ for simplicity} \tag{27a}$$

and

$$(E^{(0)}(k+K)-E^{(0)}(k))\,\chi^{(1)}(k+K)+\sum_{k_1}[v(-K)-v(k-k_1+2K)]\,(\chi^{(1)}(k_1+K)+\chi^{(1)*}(k_1-K)) = -V^{(1)}(K) \tag{27b}$$

Neglecting the exchange term $v(k-k_1+2K)$, we find that

$$\chi^{(1)}(k+K) = -\frac{V^{(1)}(K)}{\epsilon(K)}\cdot\frac{1}{E^{(0)}(k+K)-E^{(0)}(k)} \tag{27c}$$

where

$\epsilon(K)$ = RPA dielectric constant

$$= 1 + 2v(K)\sum_{k\,(occ)}\frac{1}{E^{(0)}(k+K)-E^{(0)}(k)}\cdot \tag{27d}$$

Note the appearance of HF energies everywhere. The <u>second-order energy shift</u> is

$$E^{(2)}(k) = \sum_{K_1} V^{(1)}(K_1)\chi^{(1)}(k-K_1)+\sum_{k_1}\sum_{K_1}[v(-K_1)-v(k-k_1+K_1)]\,\chi^{(1)}(k_1+K_1)\,\chi^{(1)}(k+K_1)$$

$$+\sum_{k_1}\sum_{K_1}[v(K_1)-v(k-k_1)]\,\chi^{(1)*}(k_1-K_1)\,\chi^{(1)}(k+K_1)$$

which simplifies to

$$E^{(2)}(k) = -\sum_{K_1} \left| \frac{V^{(1)}(K_1)}{\epsilon(K_1)} \right|^2 \frac{1}{E^{(0)}(k+K_1) - E^{(0)}(k)} \tag{28}$$

after neglecting the exchange terms $v(k-k_1+K_1)$ and $v(k-k_1)$. Note that the weak periodic field gets screened by the RPA dielectric constant.

Let us now do this problem using the Green's function approach but including formally more general correlations than HF. Specifically, we rederive (28) as a byproduct. To this end, we have to solve the following set of easily derived equations which are all exact:

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - V_{eff}^{(1)} \right] G(11') + i\int v(1-\bar{1})\, G(1\bar{2})\, \Gamma(\bar{2}\bar{4};\bar{3})\, K(\bar{3}\bar{1})\, G(\bar{4}1')\, d\bar{1}\, d\bar{2}\, d\bar{3}\, d\bar{4}$$

$$= \delta^{(4)}(1-1') \tag{29}$$

$$\Gamma(12;3) = -\delta^{(4)}(1-2)\,\delta^{(4)}(1-3) - i\int v(1-\bar{1})\, G(1\bar{4})\, \Gamma(\bar{4}\bar{5};3)\, G(\bar{5}\bar{2})\, \Gamma(\bar{2}2;\bar{3})\, K(\bar{3}\bar{1})$$
$$d\bar{1}\, d\bar{2}\, d\bar{3}\, d\bar{4}\, d\bar{5}$$

$$+ i\int v(1-\bar{1})\, G(1\bar{2})\, \frac{\delta\Gamma(\bar{2}2;\bar{3})}{\delta V_{eff}^{(3)}}\, K(\bar{3}\bar{1})\, d\bar{1}\, d\bar{2}\, d\bar{3} +$$

$$+ i\int v(1-\bar{1})\, G(1\bar{2})\, \Gamma(\bar{2}2;\bar{3})\, \frac{\delta K(\bar{3}\bar{1})}{\delta V_{eff}^{(3)}}\, d\bar{1}\, d\bar{2}\, d\bar{3} \tag{30}$$

$$K(12) = \delta^{(4)}(1-2) + i\int v(1-\bar{1})\, G(\bar{1}\bar{2})\, \Gamma(\bar{2}\bar{3};\bar{4})\, K(\bar{4}2)\, G(\bar{3}\bar{1}^+)\, d\bar{1}\, d\bar{2}\, d\bar{3}\, d\bar{4} \tag{31}$$

$$V_{eff}(1) = \int K(1\bar{1})\, U_{ext}(\bar{1})\, d\bar{1} \tag{32}$$

where U_{ext} is introduced only to generate the proper terms arising from the interactions between the particles. V_{eff} contains the weak periodic field, U_{ext}, and the Coulomb self energy. We now make some approximations. We take

$$\Gamma^{(0)}(12;3) = -\delta^{(4)}(1-2)\,\delta^{(4)}(1-3)\,. \tag{33}$$

It must be stressed here that this is not the usual HF approximation. Then

$$K^{(0)}(12) = \delta^{(4)}(1-2) - i\int v(1-\bar{1})\,G(\bar{1}\,\bar{2})\,K^{(0)}(\bar{2}\,2)\,G(\bar{2}\,1^{+})\,d\bar{1}\,d\bar{2} \tag{34}$$

and

$$\left[i\frac{\partial}{\partial t_1} + \frac{\nabla_1^2}{2m} - V_{eff}^{(1)}\right] G(1\,1') - i\int v(1-\bar{1})\,G(1\bar{2})\,K(\bar{2}\,\bar{1})\,G(\bar{2}\,1')\,d\bar{1}\,d\bar{2} \tag{35}$$
$$= \delta^{(4)}(1-1')\,.$$

Going to the Fourier representation we get

$$\left(\omega - \frac{k^2}{2m}\right) G(k\,k') - \sum_{k_1} V_{eff}(k_1)\,G(k-k_1;k') -$$
$$- i\sum_{k_1 k_2 k_3} v(k_1)\,G(k+k_1;k_2+k_3)\,K(k_2;k_1)\,G(k_3 k') = \delta_{kk'} \tag{36}$$

and

$$K(k\,k') = \delta_{kk'} - i\,v(k)\sum_{k_1 k_2 k_3} G(k+k_1;k_2+k_3)\,G(k_2;k_1)\,K(k_3 k')\,. \tag{37}$$

In the absence of the periodic potential and U_{ext} we have

$$G(k\,k') = G_o(k)\,\delta_{kk'}$$

being a uniform system, so that

$$K(kk') = \frac{\delta_{kk'}}{\epsilon(k)}$$

with

$$\epsilon(k) = 1 - iv(k) \sum_{k_1} G_o(k+k_1)\, G_o(k_1) \tag{38}$$

and (36) takes the form

$$\left[\omega - \frac{k^2}{2m} - i\sum_{k_1} \frac{v(k_1)}{\epsilon(k_1)}\, G^{(0)}(k+k_1)\right] G(kk') - \sum_{k_1} V_{eff}(k_1)\, G(k-k_1; k') = \delta_{kk'} .$$

Now

$$V_{eff}(k) = \sum_{K} K(k; K' V^{(1)}(K) \tag{39}$$

using only the periodic field, so that one finally has

$$\left[\omega - \frac{k^2}{2m} - M(k)\right] G(kk') - \sum_{K} \frac{V^{(1)}(K)}{\epsilon(K)}\, G(k-K, k') = \delta_{kk'} \tag{40}$$

where

$$M(k) = \text{mass operator} = i\sum_{k_1} \frac{v(k_1)}{\epsilon(k_1)}\, G^{(0)}(k+k_1) . \tag{41}$$

This is the dynamically screened exchange interaction. (k_1 here stands for the four vector.) Note also that $V^{(1)}(K)$ is statistically screened by $\epsilon(K)$, the generalized dielectric constant involving the $G^{(0)}$ which is not the HFG. Thus,

$$\left[\omega - \frac{k^2}{2m} - M(k\omega)\right] G(kk') = \delta_{kk'} + \sum_{K_1} \frac{V^{(1)}(K_1)}{\epsilon(K_1)} G(k-K_1; k') \tag{40'}$$

and

$$\left[\omega - \frac{|k-K|^2}{2m} - M(k-K\omega)\right] G(k-K; k') = \sum_{K_1} \frac{V^{(1)}(K_1)}{\epsilon(K_1)} G(k-K-K_1, k')$$

$$\approx \frac{V^{(1)}(-K)}{\epsilon(-K)} G(kk') \tag{42}$$

so that one finally has

$$\left\{\omega - \frac{k^2}{2m} - M(k\omega) - \sum_{K_1} \left|\frac{V^{(1)}(K_1)}{\epsilon(K_1)}\right|^2 \frac{1}{\omega - \frac{(k-K_1)^2}{2m} - M(k-K_1;\omega)}\right\} G(kk')$$

$$= \delta_{kk'} \ . \tag{43}$$

The poles of $G(kk')$ determine the single particle behavior. Writing the unperturbed single particle energy in the form

$$E^{(0)}(k) = \frac{k^2}{2m} + M\left(k; \frac{k^2}{2m}\right) \tag{44}$$

the modified energy due to weak periodic field away from the Brilluoin zone boundaries may be written as

$$\omega = E^{(0)}(k) - \sum_{K_1} \left|\frac{V^{(1)}(K_1)}{\epsilon(K_1)}\right|^2 \frac{1}{E^{(0)}(k-K_1) - E^{(0)}(k)} \ . \tag{45}$$

If

$$M\left(k; \frac{k^2}{2m}\right) = M_{HF}(k), \quad \epsilon(K) = 1 - iv(K) \sum_{k_1} G_{HF}^{(0)}(K+k_1)\, G_{HF}^{(0)}(k_1)$$

we recover the result obtained earlier as expression (28). At the zone boundary where

$$E^{(0)}(k) = E^{(0)}(k-K) \tag{46}$$

we examine the pole structure a little more carefully. One then neglects all other terms except this one in (43) so that the pole is now determined by the equation

$$(\omega - E^{(0)}(k))\,(\omega - E^{(0)}(k-K)) - \left| \frac{V^{(1)}(K)}{\epsilon(K)} \right|^2 = 0 \,. \tag{47}$$

If we ignore the ω dependence in M, we arrive at a familiar looking expression for the energies at the zone edge

$$\omega = \left(\frac{E^{(0)}(k) + E^{(0)}(k-K)}{2} \right) \pm \sqrt{\left(\frac{E^{(0)}(k) - E^{(0)}(k-K)}{2} \right)^2 + \left| \frac{V^{(1)}(K)}{\epsilon(K)} \right|^2} \,. \tag{48}$$

This generalizes the nearly free electron gap equation at the zone edge [6] for the interacting electron system. Recently, Tanaka [7] has also examined this problem using diagrammatic approach.

DISCUSSION

We have here constructed a perturbation method for self-consistent equations in a Green's function formulation. This is a generalization of Peng's work for static HF equations. We incidentally show that the amplitudes of the first-order wave function satisfy the usual RPA equations. As an example of the method we briefly outline a calculation of the effect of periodic field on a many-electron system.

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REFERENCES

1. H. W. Peng, Proc. Roy. Soc. (London) A178, 499 (1941).

2. C. Herring, Phys. Rev. 87, 60 (1952).

3. A. K. Rajagopal, Ph.D. Thesis, Harvard University, Cambridge, Massachusetts, July 1964. See also ARPA Technical Report No. 11, August, 1964 with H. Brooks and N. R. Ranganathan.

4. D. J. Thouless, Nucl. Phys. 21, 225 (1960).

5. J. C. Slater, Quantum Theory of Atomic Structure, Vol. 1, Chap. 5, McGraw-Hill Book Co., New York, 1960.

6. P. W. Anderson, Concepts in Solids, Chap. 2, Sec. B1, W. A. Benjamin and Co., New York, 1963.

7. M. Tanaka, Progr. Theoret. Phys. (Japan) 29, 675 (1963).

8. N. Fukuda, Nucl. Phys. 44, 553 (1963).