Many Electron Theory:

Polarization propagator.

Continued notes for a workgroup September-October 2002.

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Polarization propagators as matrix forms.

Response functions were considered earlier within the Hartree-Fock framework. We revisit this case in the general formalism of Green functions. Thus one considers operators of the form

$$A^\dagger = \sum_{rs} a_r^\dagger a_s c_{rs}$$

and the forms

$$\left\langle\left\langle A\ ;A^\dagger\right\rangle\right\rangle_E = \frac{1}{E}\left\langle\left[A,A^\dagger\right]_-\right\rangle + \frac{1}{E^2}\left\langle\left[\left[A,H\right],A^\dagger\right]_-\right\rangle + \frac{1}{E^2}\left\langle\left\langle\left[A\ ,H\right];A^\dagger\right\rangle\right\rangle_E$$

It follows that

$$\begin{aligned}\left\langle\left[A,A^\dagger\right]_-\right\rangle &= \sum_{rr'ss'} c_{rs}^* \left\langle\left[a_s^\dagger a_r, a_{r'}^\dagger a_{s'}\right]_-\right\rangle c_{r's'} \\ &= \sum_{rr'ss'} c_{rs}^* \left(\delta_{rr'}\left\langle a_s^\dagger a_{s'}\right\rangle - \delta_{ss'}\left\langle a_{r'}^\dagger a_r\right\rangle\right) c_{r's'} \\ &= \sum_{rss'}\left(c_{rs}^* c_{rs'} - c_{s'r}^* c_{sr}\right)\rho_{s's}\end{aligned}$$

as well as

$$\left\langle\left[\left[A,H\right],A^\dagger\right]_-\right\rangle = \sum_{rr'ss'} c_{rs}^* \Omega_{rs,r's'} c_{r's'}$$

$$\begin{aligned}\Omega_{rs,r's'} &= h_{rr'}\rho_{s's} + \sum_{uv}\left[(rr'\,|\,uv) - (rv\,|\,ur')\right]\Gamma(s'v;su) \\ &+ h_{s's}\rho_{rr'} + \sum_{uv}\left[(s's\,|\,uv) - (s'v\,|\,us)\right]\Gamma(rv;r'u) \\ &- \delta_{s's}\sum_u h_{ru}\rho_{ur'} - \delta_{s's}\sum_{tuv}(rt\,|\,uv)\Gamma(tv;r'u) \\ &- \delta_{rr'}\sum_u \rho_{s'u}h_{us} - \delta_{rr'}\sum_{tuv}(ts\,|\,uv)\Gamma(s'v;tu) \\ &- \sum_{uv}(ru\,|\,s'v)\Gamma(uv;sr') + \sum_{uv}(vs\,|\,ur')\Gamma(s'r;vu)\end{aligned}$$

$$\Gamma(rs;vu) \equiv \left\langle a_v^\dagger a_u^\dagger a_s a_r\right\rangle$$

The Ω-matrix is similar to the stability matrix in the Hartree-Fock matrix but is here defined as an average over a general ensemble, possibly including correlation. The two-particle matrix Γ differs from Löwdin's definition by a factor of two. The rather unwieldy expression is more

readily examined when the one particle matrix is diagonal, e. g. when the basis is the natural spin orbitals. The two particle matrix is also written as an "independent particle" part and a correlation correction. Thus

$$\rho_{rs} = \left\langle a_s^\dagger a_r \right\rangle = \delta_{rs} n_s;$$

$$\Gamma(pq;rs) = \left\langle a_r^\dagger a_s^\dagger a_q a_p \right\rangle$$

$$= \left\langle a_r^\dagger a_p \right\rangle \left\langle a_s^\dagger a_q \right\rangle - \left\langle a_r^\dagger a_q \right\rangle \left\langle a_s^\dagger a_p \right\rangle + \Gamma_c(pq;rs)$$

$$= \left(\delta_{rp}\delta_{sq} - \delta_{rq}\delta_{sp}\right) n_r n_s + \Gamma_c(pq;rs)$$

Spin orbital occupation numbers are here not necessarily zero or unity. They can attain values between these limits.

The Ω-matrix will have an "independent particle" part and a correlation part as well and we write

$$\Omega_{rs,r's'} = f_{rr'}\delta_{s's}\left(n_s - n_{r'}\right) - f_{s's}\delta_{rr'}\left(n_{s'} - n_r\right)$$

$$+\left[(rs \mid s'r') - (rr' \mid s's)\right]\left(n_s - n_{r'}\right)\left(n_{s'} - n_r\right) + \hat{\Omega}_{rs,r's'}$$

$$f_{rr'} = h_{rr'} + \sum_s \left[(rr' \mid ss) - (rs \mid r's)\right] n_s$$

A hat marks the correlation part and a generalized Fock matrix notation is used. The Hartree-Fock stability matrix is recovered for canonical spin orbitals and integer occupation numbers. Our sesquilinear hermitean form $\sum_{rr'ss'} c_{rs}^* \Omega_{rs,r's'} c_{r's'}$ is nonnegative for a stable ensemble and it is possible to define a basis of operators so that

$$\left\langle \left[\left[A_\mu, H\right], A_\nu^\dagger\right]_- \right\rangle = \delta_{\mu\nu}$$

There will generally be fewer operators in the set $\left\{A_\nu^\dagger|\nu=1,2,\ldots\right\}$ than in the set $\left\{a_r^\dagger a_s|r,s=1,2,\ldots M\right\}$ and there will be no complete expansion of the latter set of operators in the former. We observe further that

$$\left\langle\left[\left[A_\mu,H\right],A_\nu^\dagger\right]_-\right\rangle=\left\langle\left[\left[A_\nu^\dagger,H\right],A_\mu\right]_-\right\rangle+\left\langle\left[\left[A_\mu,A_\nu^\dagger\right],H\right]_-\right\rangle=\left\langle\left[\left[A_\nu^\dagger,H\right],A_\mu\right]_-\right\rangle$$

since the ensemble is stable towards distortions.

A unitary transformation within the set $\left\{A_\nu^\dagger|\nu=1,2,\ldots\right\}$ does not change the orthogonality and normalization of these operators. Such a transformation can be chosen to diagonalize the hermitean matrix

$$\left\{\left\langle\left[A_\mu,A_\nu^\dagger\right]_-\right\rangle\right\}=\left\{\delta_{\mu\nu}\lambda_\mu\right\}$$

where it should be noted that the eigenvalues have the dimension inverse energy, thus proportional to wavelength. It follows that since

$$\left\langle\left[A_\nu^\dagger,A_\mu\right]_-\right\rangle=-\left\langle\left[A_\mu,A_\nu^\dagger\right]_-\right\rangle=-\delta_{\mu\nu}\lambda_\mu$$

eigenvalues are paired, unless they equal zero. We reserve the creator (excitation) notation for those operators with positive eigenvalues and use the annihilator (deexcitation) expression for the corresponding negative values.

A general operator of the form above may be expanded in the set we have defined:

$$A^\dagger=\sum_\nu\left[A_\nu^\dagger\left\langle\left[\left[A_\nu,H\right],A^\dagger\right]_-\right\rangle+A_\nu\left\langle\left[\left[A_\nu^\dagger,H\right],A^\dagger\right]_-\right\rangle\right]+\delta A^\dagger$$

The remainder, $\delta A^{\dagger}$, does not have any operators within the operator space spanned by the set used and cannot contribute in the calculations above. We find then that

$$\left\langle \left[A, A^{\dagger} \right]_{-} \right\rangle = \sum_{\nu} \lambda_{\nu} \left\{ \left| \left\langle \left[\left[A_{\nu}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2} - \left| \left\langle \left[\left[A_{\nu}^{\dagger}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2} \right\}$$

$$\left\langle \left[\left[A, H \right], A^{\dagger} \right]_{-} \right\rangle = \sum_{\nu} \left\{ \left| \left\langle \left[\left[A_{\nu}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2} + \left| \left\langle \left[\left[A_{\nu}^{\dagger}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2} \right\}$$

and assert the approximation for the propagator:

$$\left\langle \left\langle A \; ; A^{\dagger} \right\rangle \right\rangle_{E} = \sum_{\nu} \left\{ \frac{\left| \lambda_{\nu} \left\langle \left[\left[A_{\nu}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2}}{E\lambda_{\nu} - 1} - \frac{\left| \lambda_{\nu} \left\langle \left[\left[A_{\nu}^{\dagger}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2}}{E\lambda_{\nu} + 1} \right\}$$

We are led to the interpretation that the eigenvalues $\left\{ \lambda_{\nu} \right\}$ are proportional to the wavelengths for excitation and absorption in the system. The zero temperature, non-degenerate ground state admits the identification of matrix elements such that

$$\frac{\left| \lambda_{\nu} \left\langle \left[\left[A_{\nu}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2}}{\lambda_{\nu}} = \left| \left\langle \nu \left| A^{\dagger} \right| 0 \right\rangle \right|^{2}; \frac{\left| \lambda_{\nu} \left\langle \left[\left[A_{\nu}^{\dagger}, H \right], A^{\dagger} \right]_{-} \right\rangle \right|^{2}}{\lambda_{\nu}} = \left| \left\langle 0 \left| A^{\dagger} \right| \nu \right\rangle \right|^{2};$$

and, accordingly, it shall hold that

$$A_{\nu}^{\dagger} |0\rangle = |\nu\rangle \sqrt{\lambda_{\nu}}; A_{\nu} |0\rangle = 0.$$

It has proven difficult to construct a self consistent procedure that ensures the annihilation condition. It was shown by Öhrn and myself that an *antisymmetrized geminal power state*, |AGP>, is required when operators of the lowest order only are included in the calculation. Thus

$$|0\rangle = |AGP\rangle = \left(\sum_{rs} a_{r}^{\dagger} a_{s}^{\dagger} p_{rs} \right)^{N/2} |vac\rangle$$

can be a proper representation of the ground state but it remains unclear whether a self consistent procedure for its determination can be constructed for a general hamiltonian. Nevertheless, the kind of approximation considered here has given many good results, both in the simplest form with the Hartree-Fock state and with more involved approximations to the ground state.

It seems that the first application of the random phase approximation or, equivalently, the linearized time dependent Hartree-Fock method to molecular problems was by Ball and McLachlan in the early sixties. Robert Harris, Vincent McKoy and Shibuya, Jørgensen and myself showed the efficacy of the method in the late sixties. Higher order developments took place in the seventies pioneered by Jørgensen, Oddershede and Mark Ratner who attempted self-consistent calculations. Oddershede pushed the *Second Order Polarization Propagator Approach, SOPPA,* and made this a viable method for response functions such as they appear in indirect spin-spin coupling constants and other magnetic problems. Responses of higher order, like hyperpolarizabilities, have been calculated by Jørgensen and collaborators and are a part of the program complex Dalton.

Calculations with *AGP*-states showed quite satisfactory results in the early eighties when Hans Jørgen Aagaard Jensen, Brian Weiner and Yngve Öhrn implemented them at Florida. Optimization of the reference state proved awkward and slow and development was set on hold. Renewed efforts by Weiner and Ortiz may offer a new start..

Number non-conserving approximations.

Superconductivity and various magnetic materials have been described in terms of states that are not eigenstates of some symmetry operators, even when these do commute with the hamiltonian. Antiferromagnetic states are perceived as having positive and negative spin density on alternating sites even though the true ground state is a pure singlet state. The phenomenon of superconductivity resisted a theoretical description for some fifty years until Bardeen, Cooper, and Schrieffer came up with a useful model. Their formulation was later reformulated in a propagator form by Nambu, who considered combinations of creation and annihilation operators and disregarded the conservation of electrons. The BCS *ansatz* is based on the presence of an effective attraction between electron mediated by the lattice phonons that overcomes the Coulomb repulsion.

The argument starts with the consideration of a general form for the operator:

$$A^\dagger = \sum_s \left(a_s^\dagger c_s + a_{-s} c_{-s} \right)$$

Again we use the notation that negative indices relate to negative spin. The moment expansion will consider the option of number fluctuations and we use the effective hamiltonian $H - \mu N$. We calculate

$$\left\langle \left[A, A^\dagger \right]_+ \right\rangle = \sum_s \left(c_s^* c_s + c_{-s}^* c_{-s} \right)$$

$$\left\langle \left[\left[A, H \right], A^\dagger \right]_+ \right\rangle = \sum_{rs} \left(c_r^* f_{rs} c_s + c_r^* \hat{f}_{r-s} c_{-s} + c_{-r}^* \hat{f}_{-rs} c_s + c_{-r}^* \hat{f}_{-r-s} c_{-s} \right)$$

and use the notations relating to the previous ones. Detailed forms are

$$f_{rs} = h_{rs} - \mu\delta_{rs} + \sum_{uv}\left\{\left[(rs\,|\,uv) - (rv\,|\,us)\right]\left\langle a_u^\dagger a_v\right\rangle + (rs\,|\,-u-v)\left\langle a_{-u}^\dagger a_{-v}\right\rangle\right\}$$

$$\hat{f}_{r-s} = \left\langle\left[\left[a_r, H\right], a_{-s}\right]_+\right\rangle = \sum_{uv}(ru\,|\,-s-v)\left\langle a_{-v}a_u\right\rangle$$

$$\hat{f}_{-rs} = \left\langle\left[\left[a_{-r}^\dagger, H\right], a_s^\dagger\right]_+\right\rangle = \sum_{uv}(-v-r\,|\,us)\left\langle a_u^\dagger a_{-v}^\dagger\right\rangle = \hat{f}_{s-r}^*$$

$$\hat{f}_{-r-s} = -h_{-s-r} + \mu\delta_{-s-r}$$
$$-\sum_{uv}\left\{\left[(-s-r\,|\,-v-u) - (-v-r\,|\,-s-u)\right]\left\langle a_{-v}^\dagger a_{-u}\right\rangle + (-s-r\,|\,vu)\left\langle a_v^\dagger a_u\right\rangle\right\}$$

The forms above lead to a hermitean eigenvalue problem with twice the dimension of the normal, spin restricted Hartree-Fock form. Vanishing expectation values $\langle a_{-v}a_u\rangle$ bring us back to the traditional form with separate eigenvalue equations for positive and negative spin.

Number conservation "turned off" opens for a more general type of propagator. It should be noted that an initial spin balanced Hartree-Fock solution gives a spectrum for the $\left\{\hat{f}_{-r-s}\right\}$ which is the "mirror" image of that of $\left\{f_{rs}\right\}$ and that even a small interaction $\left\{\hat{f}_{r-s}\right\}$ may cause a change in the original levels when $\varepsilon_r - \mu \approx \mu - \varepsilon_{-s}$.

Discussions of the conditions for "pairing" and its relevance for superconductivity can be found in the literature in solid state physics, e. g. Kittel's and/or Ziman's textbooks. The Nambu formalism is also in Nozières book.

The new superconducting materials have yet to receive a satisfactory theoretical analysis, as I understand it.

Basic features of the number symmetry breaking approximation are exhibited by considering a canonical basis for the Fock matrix:

$$f_{rs} = \delta_{rs}\left(\varepsilon_r - \mu\right);\ f_{-s-r} = \delta_{-s-r}\left(\mu - \varepsilon_{-s}\right);$$

and a simple form of the coupling between a spin orbital below the Fermi level and one above. Thus we define a new set of operators for the coupled spin orbitals

$$A_r^\dagger = a_r^\dagger \cos\vartheta + a_{-s} e^{i\varphi} \sin\vartheta;\ A_{-s} = -a_r^\dagger e^{-i\varphi} \sin\vartheta + a_{-s} \cos\vartheta;$$

and require that

$$\begin{Bmatrix} \left\langle \left[\left[A_r, H\right], A_r^\dagger\right]_+ \right\rangle & \left\langle \left[\left[A_r, H\right], A_{-s}\right]_+ \right\rangle \\ \left\langle \left[\left[A_{-s}^\dagger, H\right], A_r^\dagger\right]_+ \right\rangle & \left\langle \left[\left[A_{-s}^\dagger, H\right], A_{-s}\right]_+ \right\rangle \end{Bmatrix} =$$

$$\begin{Bmatrix} \varepsilon_r - \mu - \Delta\sin^2\vartheta & 0 \\ 0 & \mu - \varepsilon_{-s} + \Delta\sin^2\vartheta \end{Bmatrix}$$

Here appear the entity Δ and the angle ϑ. They are defined as

$$\Delta = \sqrt{\left(\mu - \tfrac{1}{2}\varepsilon_r - \tfrac{1}{2}\varepsilon_{-s}\right)^2 + \left|f_{r-s}\right|^2};$$

$$\vartheta = \tfrac{1}{2}\arcsin\left(\frac{\left|f_{r-s}\right|}{\Delta}\right);\ 0 \le \vartheta \le \tfrac{\pi}{4};$$

All levels are stabilized:

$$\varepsilon_r \to \varepsilon_r - \Delta\sin^2\vartheta;\ \varepsilon_{-s} \to \varepsilon_{-s} - \Delta\sin^2\vartheta;$$

This can only be consistent