Many Electron Theory:

Green functions.

Continued notes for a workgroup September-October 2002.

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Green functions in the energy representation.

George Green, whose name is attached to the quantities to be studied, transformed the differential equations of electromagnetics into integral equations by means of kernels that have attained the generic name Green functions. An original one is the Coulomb potential, the Green function of the Poisson equation. Scattering theory, particularly in the Born type approximation, employs Green functions, and many-body theory has shown their general versatility. It is most often the case that the argument starts from a time-dependent formulation and that a subsequent Fourier transformation generates the energy representation, the spectral forms, and analytical features.

These notes departs from the energy representation of a general Green function or propagator in its spectral form. A hamiltonian, its eigenstates, and an ensemble for the formation of average values should be specified. Two operators, *A* and *B*, are considered and the definition

$$\langle\langle A;B\rangle\rangle_E = \sum_{m,n}\langle m|A|n\rangle\langle n|B|m\rangle\left[\frac{\rho_m}{E-E_n+E_m+i\eta} \pm \frac{\rho_n}{E-E_n+E_m-i\eta}\right]$$

is used. The probability to find the state *m* in the ensemble is given by ρ_m and infinitesimal imaginary parts are added in the denominators in order to specify the boundary conditions in the time domain. An alternative form is

$$\langle\langle A;B\rangle\rangle_E = \sum_{m,n}\rho_m\left[\frac{\langle m|A|n\rangle\langle n|B|m\rangle}{E-E_n+E_m+i\eta} \pm \frac{\langle m|B|n\rangle\langle n|A|m\rangle}{E-E_m+E_n-i\eta}\right]$$

This function exhibits poles in the complex energy plane for system energy differences where the operators give non vanishing matrix elements. The sign between the terms is optional. It will be chosen to simplify equations.

It is useful to consider the Green function as a function in the complex energy plane. We leave the detailed structure near the real axis and attempt to calculate the form

$$\langle\langle A;B\rangle\rangle_E = \sum_{m,n}\rho_m\left[\frac{\langle m|A|n\rangle\langle n|B|m\rangle}{E-E_n+E_m} \pm \frac{\langle m|B|n\rangle\langle n|A|m\rangle}{E-E_m+E_n}\right]$$

The identities

$$\begin{aligned}\frac{\langle m|A|n\rangle\langle n|B|m\rangle}{E-E_n+E_m} &= \frac{\langle m|A|n\rangle\langle n|B|m\rangle}{E} + \frac{\langle m|A|n\rangle\left(E_n-E_m\right)\langle n|B|m\rangle}{E\left(E-E_n+E_m\right)} \\ &= \frac{\langle m|A|n\rangle\langle n|B|m\rangle}{E} + \frac{\langle m|[A,H]|n\rangle\langle n|B|m\rangle}{E\left(E-E_n+E_m\right)} \\ &= \frac{\langle m|A|n\rangle\langle n|B|m\rangle}{E} + \frac{\langle m|A|n\rangle\langle n|[H,B]|m\rangle}{E\left(E-E_n+E_m\right)}\end{aligned}$$

allow us to write

$$\langle\langle A;B\rangle\rangle_E = \frac{\langle[A,B]_\pm\rangle}{E} + \frac{1}{E}\langle\langle[A,H];B\rangle\rangle_E = \frac{\langle[A,B]_\pm\rangle}{E} + \frac{1}{E}\langle\langle A;[H,B]\rangle\rangle_E$$

These equations are often called "equations of motion" since they derived from the Heisenberg picture of time-dependent operators.

The electronic hamiltonian will, when commuted with some arbitrary operator, yield more and more complicated expressions and it is therefore mandatory to truncate the series at some point. The relevance and inherent justification of such truncations cannot be determined by abstract arguments.

Consider the operator $A^\dagger = \sum_s a_s^\dagger c_s = B$ and its adjoint, as the ones in the Green function. It is then most useful to consider the upper sign between the terms in the spectral form. The equations above lead to the form

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

Here it holds that

$$\left\langle\left[A,A^{\dagger}\right]_+\right\rangle = \sum_{rs} c_r^*\left(\delta_{rs} + S_{rs}\right)c_s$$

$$\left\langle\left[\left[A,H\right],A^{\dagger}\right]_+\right\rangle = \sum_{rs} c_r^* f_{rs} c_s$$

and the elements of the Fock matrix occur again. A choice of coefficients that corresponds to a canonical Hartree-Fock spin orbital gives

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

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

Neglect of the last bracket leaves us with the Hartree-Fock approximation to the *one electron propagator*. The general form obtains as the matrix expression

$$\mathbf{G}(E) = \left\{\left\langle\left\langle a_r\,;a_s^{\dagger}\right\rangle\right\rangle_E\right\} = (\mathbf{1}+\mathbf{S})\left[E(\mathbf{1}+\mathbf{S}) - \mathbf{f}\right]^{-1}(\mathbf{1}+\mathbf{S})$$

A zero temperature, not degenerate, ground state offers the classification of the spin orbital energies as being below or above some suitable value, the Fermi energy. Density matrix elements are then obtained from a contour integral in the complex energy plane that encloses the occupied values:

$$\rho = \tfrac{1}{2\pi i}\oint dE\,\mathbf{G}(E) = \left\{\left\langle a_s^{\dagger}a_r\right\rangle\right\}$$

Charles Coulson realized this relation for the Hückel model and used it with great advantage for many an analysis.

Interpretation of the poles of the electron propagator support the findings of Koopmans, but the Hartree-Fock approximation cannot account for many of the finer details of photoelectron spectra and it is particularly of little use for the study of anions. Higher order formulations are then called for and we consider the general form

$$A^\dagger = \sum_s a_s^\dagger c_s + \sum_{prs} a_p^\dagger a_r^\dagger a_s c_{prs} + \ldots$$

This kind of an operator is interpreted as adding an electron and creating an excitation in the system and possibly creating a more favorable situation for attachment. Its adjoint can remove an electron and excite the residual system.

Matrix formulations are useful in order to examine the higher order electron propagator options. We introduce the notation

$$A^\dagger = \sum_s a_s^\dagger c_s + \sum_\nu b_\nu^\dagger c_\nu$$

where the new operators $b_\nu^\dagger$ are forms as those indicated above, products of elementary operators and one creation operator more than the number of annihilation operators. The set of creation operators are arranged as a partitioned row vector:

$$\left\{\mathbf{a}^\dagger;\mathbf{b}^\dagger\right\} = \left\{a_1^\dagger, a_2^\dagger, \ldots; b_1^\dagger, b_2^\dagger, \ldots\right\}$$

while the corresponding annihilation operators form a column vector. A matrix Green function is then written as

$$\left\langle\left\langle \begin{Bmatrix}\mathbf{a}\\ \mathbf{b}\end{Bmatrix}; \begin{Bmatrix}\mathbf{a}^\dagger & \mathbf{b}^\dagger\end{Bmatrix} \right\rangle\right\rangle_E = \begin{Bmatrix} \left\langle\left\langle \mathbf{a} ; \mathbf{a}^\dagger \right\rangle\right\rangle_E & \left\langle\left\langle \mathbf{a} ; \mathbf{b}^\dagger \right\rangle\right\rangle_E \\ \left\langle\left\langle \mathbf{b} ; \mathbf{a}^\dagger \right\rangle\right\rangle_E & \left\langle\left\langle \mathbf{b} ; \mathbf{b}^\dagger \right\rangle\right\rangle_E \end{Bmatrix}$$

The upper left corner block is the electron propagator, the other blocks are readily interpreted from the spectral representation.

Our previous procedure, which considers the moment expansion, requires the matrices

$$\mathbf{M} = \begin{Bmatrix} \left\langle \left[\mathbf{a} \ , \mathbf{a}^\dagger \right]_+ \right\rangle & \left\langle \left[\mathbf{a} \ , \mathbf{b}^\dagger \right]_+ \right\rangle \\ \left\langle \left[\mathbf{b} \ , \mathbf{a}^\dagger \right]_+ \right\rangle & \left\langle \left[\mathbf{b} \ , \mathbf{b}^\dagger \right]_+ \right\rangle \end{Bmatrix} = \begin{Bmatrix} \mathbf{M}_{aa} & \mathbf{M}_{ab} \\ \mathbf{M}_{ba} & \mathbf{M}_{bb} \end{Bmatrix}$$

and

$$\mathbf{F} = \begin{Bmatrix} \left\langle \left[\left[\mathbf{a} \ , H \right], \mathbf{a}^\dagger \right]_+ \right\rangle & \left\langle \left[\left[\mathbf{a} \ , H \right], \mathbf{b}^\dagger \right]_+ \right\rangle \\ \left\langle \left[\left[\mathbf{b} \ , H \right], \mathbf{a}^\dagger \right]_+ \right\rangle & \left\langle \left[\left[\mathbf{b} \ , H \right], \mathbf{b}^\dagger \right]_+ \right\rangle \end{Bmatrix} = \begin{Bmatrix} \mathbf{F}_{aa} & \mathbf{F}_{ab} \\ \mathbf{F}_{ba} & \mathbf{F}_{bb} \end{Bmatrix}$$

A regular hermitean eigenvalue problem obtains when the metric matrix **M** is positive definite. The matrix Green function is then given by the form

$$\left\langle \left\langle \begin{Bmatrix} \mathbf{a} \\ \mathbf{b} \end{Bmatrix}; \begin{Bmatrix} \mathbf{a}^\dagger & \mathbf{b}^\dagger \end{Bmatrix} \right\rangle \right\rangle_E = \mathbf{M}(E\mathbf{M} - \mathbf{F})^{-1}\mathbf{M}$$

It is seen that the matrix elements of the metric matrix and of the "dynamic" matrix **F** depend on operator expectation values, just as is the case for the Hartree-Fock approximation. The problem of finding a self-consistent solution is generally a complex one. A certain choice of additional operators $b_\nu^\dagger$ may provide a positive definite matrix in one iteration but not in the next. It is required to examine the consequences carefully in order to maintain sensible results.

We consider in further detail the situation that the metric matrix has vanishing blocks off the diagonal and the basis is orthonormal. The inverse matrix, in the partitioned form is then

$$(E\mathbf{M}-\mathbf{F})^{-1}=\begin{Bmatrix} E\mathbf{1}-\mathbf{F}_{aa} & -\mathbf{F}_{ab} \\ -\mathbf{F}_{ba} & E\mathbf{M}_{bb}-\mathbf{F}_{bb} \end{Bmatrix}^{-1} \equiv \begin{Bmatrix} \mathbf{G}_{aa}(E) & \mathbf{G}_{ab}(E) \\ \mathbf{G}_{ba}(E) & \mathbf{G}_{bb}(E) \end{Bmatrix}$$

$$\mathbf{G}_{aa}(E)=\left[E\mathbf{1}-\mathbf{F}_{aa}-\mathbf{F}_{ab}\left(E\mathbf{M}_{bb}-\mathbf{F}_{bb}\right)^{-1}\mathbf{F}_{ba}\right]^{-1}$$

$$\mathbf{G}_{ba}(E)=\left(E\mathbf{M}_{bb}-\mathbf{F}_{bb}\right)^{-1}\mathbf{F}_{ba}\mathbf{G}_{aa}(E)$$

$$\mathbf{G}_{ab}(E)=\mathbf{G}_{aa}(E)\mathbf{F}_{ba}\left(E\mathbf{M}_{bb}-\mathbf{F}_{bb}\right)^{-1}$$

$$\mathbf{G}_{bb}(E)=\left[E\mathbf{M}_{bb}-\mathbf{F}_{bb}-\mathbf{F}_{ba}\left(E\mathbf{1}-\mathbf{F}_{aa}\right)^{-1}\mathbf{F}_{ab}\right]^{-1}$$

The electron propagator matrix is the top left corner block and we observe that the Fock operator is now supplemented by an additional term called the self energy Σ(E):

$$\Sigma(E)=\mathbf{F}_{ab}\left(E\mathbf{M}_{bb}-\mathbf{F}_{bb}\right)^{-1}\mathbf{F}_{ba}$$

The presence of poles in the self energy operator will influence the poles of the electron propagator and the corresponding residues. Basic Hartree-Fock theory gives residues of unity in the canonical spin orbital basis.

We examine the case that the operators $b_\nu^\dagger$ are chosen from the set $\left\{a_p^\dagger a_r^\dagger a_s\right\}$. Metric matrix elements in the blocks $\mathbf{M}_{ab}$ and $\mathbf{M}_{ba}$ require density matrix elements while those in $\mathbf{M}_{bb}$ depend upon expectation values such as $\left\langle a_p^\dagger a_q^\dagger a_r a_s\right\rangle$, e. g. the second order density matrix. Elements in the blocks $\mathbf{F}_{ab}$ and $\mathbf{F}_{ba}$ also include these elements. The block $\mathbf{F}_{bb}$ involves density matrix elements up to the third order: $\left\langle a_p^\dagger a_q^\dagger a_r^\dagger a_s a_t a_u\right\rangle$. All of these can be calculated from the matrix Green function, with some effort, and self consistency may be ascertained.

A self consistent matrix Green function does not by itself assure the so called *N*-representability. That is, a ground state cannot necessarily be constructed so that it satisfies the annihilation conditions. The poles of the propagator matrix corresponds to operators $A^\dagger$ such that

$$\left\langle \left[A, A^\dagger \right]_+ \right\rangle = 1; \left\langle \left[[A, H], A^\dagger \right] \right\rangle = \varepsilon.$$

A pole below the Fermi energy will then require that $A^\dagger|0\rangle = 0$ and one above needs $A|0\rangle = 0$.

Perturbation theory has been used as a guideline for the higher order approximations to the Green functions. Expectation values are then computed from approximations to the ground state from perturbation theory or from coupled cluster forms of the ground state.

Work on the electron propagator in the form presented here was pioneered at Florida in Yngve Öhrn´s group. Papers by Öhrn and his students George Purvis, Greg Born, and particularly Vince Ortiz established the feasibility of these calculations. Ortiz has carried the work in recent years and established himself as the expert. His methods are incorporated in the Gaussian packages.

Other, early, contributors to this field are Lorenz Cederbaum, Wolfgang Domcke, Barry Pickup, and Osvaldo Goscinski. The solid state community has generally been leaning towards the methods developed from diagrammatic perturbation expansions, notably by Lars Hedin.