

Many Electron Theory:

Second Quantization, perturbation theory, propagators

Notes prepared for a seminar series August to October 2002.

Some literature:

An unusual reference.

H. C. Longuet-Higgins, in *Quantum Theory of Atoms and Molecules*, A TRIBUTE TO JOHN C. SLATER, Ed. P.-O- Löwdin, Academic Press 1966, p. 105.

On temperature dependent perturbation theory:

See e. g. J. Linderberg and Y. Öhrn, *Propagators in Quantum Chemistry*, Academic Press 1973, Chapter 13.

On coupled clusters:

See e.g. F. E. Harris, H. J. Monkhorst, and D. L Freeman, *Algebraic and Diagrammatic Methods in Many-Fermion Theory*, Oxford 1992, p. 313ff.

Concepts from set theory:

Consider the basis of spin orbitals, $u_s(\xi) = \begin{Bmatrix} u_{s\alpha}(\mathbf{r}) \\ u_{s\beta}(\mathbf{r}) \end{Bmatrix}$, as members of a set

with M elements:

$$B: \{u_s | s = 1, 2, \dots, M\}$$

The *power set* of B is the set of all subsets of B :

$$P(B): \left\{ \Phi_K \mid K = (s_1, s_2, \dots, s_N); u_{s_j} \in B, j = 1, 2, \dots, N; N = 0, 1, \dots, M \right\}$$

The elements of the power set are a map of the set of Slater determinants that can be formed from a basis of M spin orbitals. These elements are the basis for a graded Hilbert space called Fock space, or occupation numbers space. They are often represented as kets and bras:

$$|K\rangle = |s_1, s_2, \dots, s_N\rangle; \langle K| = \langle s_1, s_2, \dots, s_N|$$

Operators in this space are represented in terms of elementary shift operators between elements that differ in one basis element.

Creation and annihilation:

The sets of *creation* operators: $\{a_s^\dagger | s = 1, 2, \dots, M\}$ and *annihilation* operators: $\{a_s | s = 1, 2, \dots, M\}$ have by definition an algebra which is generated from the basic *anticommutation* relations:

$$\begin{aligned} a_r^\dagger a_s^\dagger + a_s^\dagger a_r^\dagger &= [a_r^\dagger, a_s^\dagger]_+ = 0; \\ a_r a_s + a_s a_r &= [a_r, a_s]_+ = 0; \\ a_r a_s^\dagger + a_s^\dagger a_r &= [a_r, a_s^\dagger]_+ = \delta_{rs} + S_{rs}; \\ \delta_{rs} + S_{rs} &= \int d\mathbf{r} \left\{ u_{r\alpha}^*(\mathbf{r}), u_{r\beta}^*(\mathbf{r}) \right\} \left\{ \begin{matrix} u_{s\alpha}(\mathbf{r}) \\ u_{s\beta}(\mathbf{r}) \end{matrix} \right\} \\ &= \int d\mathbf{r} \left[u_{r\alpha}^*(\mathbf{r}) u_{s\alpha}(\mathbf{r}) + u_{r\beta}^*(\mathbf{r}) u_{s\beta}(\mathbf{r}) \right] \end{aligned}$$

The overlap integrals S_{rs} equal zero for an orthonormal basis.

An entity called the *vacuum* state has the property that any annihilation operator destroys it:

$$a_s |vac\rangle = 0; \forall s$$

Products of creation operators applied to the vacuum state generate elements of the Fock space:

$$|pq\dots n\rangle = a_p^\dagger a_q^\dagger \dots a_n^\dagger |vac\rangle$$

These *kets* have associated *bras* in Dirac's nomenclature:

$$\langle pq\dots n| = \langle vac|a_n\dots a_q a_p$$

and a *metric* is found from simple algebra:

$$\langle r|s\rangle = \langle vac|a_r a_s^\dagger|vac\rangle = \langle vac|\delta_{rs} + S_{rs} - a_s^\dagger a_r|vac\rangle = \delta_{rs} + S_{rs}.$$

The vacuum state is assumed to be normalized: $\langle vac|vac\rangle = 1$.

More involved metric elements are found by means of an induction argument:

$$\begin{aligned} \langle pq\dots n|p'q'\dots n'\rangle &= \langle q\dots n|a_p a_{p'}^\dagger|q'\dots n'\rangle \\ &= \langle q\dots n|\delta_{pp'} + S_{pp'} - a_{p'}^\dagger a_p|q'\dots n'\rangle \\ &= (\delta_{pp'} + S_{pp'})\langle q\dots n|q'\dots n'\rangle - \langle q\dots n|a_{p'}^\dagger a_p a_{q'}^\dagger|\dots n'\rangle \\ &= (\delta_{pp'} + S_{pp'})\langle q\dots n|q'\dots n'\rangle \\ &\quad - (\delta_{pq'} + S_{pq'})\langle q\dots n|q'\dots n'\rangle + \langle q\dots n|a_{p'}^\dagger a_{q'}^\dagger a_p|\dots n'\rangle \\ &= (\delta_{pp'} + S_{pp'})\langle q\dots n|q'\dots n'\rangle \\ &\quad - (\delta_{pq'} + S_{pq'})\langle q\dots n|p'\dots n'\rangle + \dots \end{aligned}$$

that is by "pairing off" the spin orbital p annihilation operator with each of the creation operators in the ket the matrix element is reduced to a sum of elements of one less operator in both the bra and the ket. The final result is that the element comes out as the determinant of the basic anticommutation elements:

$$\langle pq \dots n | p' q' \dots n' \rangle = \begin{vmatrix} \delta_{pp'} + S_{pp'} & \delta_{pq'} + S_{pq'} & \dots & \delta_{pn'} + S_{pn'} \\ \delta_{qp'} + S_{qp'} & \delta_{qq'} + S_{qq'} & \dots & \delta_{qn'} + S_{qn'} \\ \vdots & \vdots & \ddots & \vdots \\ \delta_{np'} + S_{np'} & \delta_{nq'} + S_{nq'} & \dots & \delta_{nn'} + S_{nn'} \end{vmatrix}$$

and it is evident that the number of rows has to equal the number of columns in order not to end with a nil result. Compare with the properties of the Slater determinants. A transposition of two rows or two columns gives a sign change.

Just as we can consider a map of the basis B on a another one, B' , in terms of a linear substitution:

$$\phi_k = \sum_s u_s C_{sk}$$

We introduce a map where

$$|k\rangle = \tilde{a}_k^\dagger |vac\rangle = \sum_s |s\rangle C_{sk} = \left(\sum_s a_s^\dagger C_{sk} \right) |vac\rangle$$

and define a similarity transformation such that

$$e^T a_s^\dagger e^{-T} = a_s^\dagger + [T, a_s^\dagger] + \frac{1}{2} [T, [T, a_s^\dagger]] + \dots = \sum_s a_s^\dagger C_{sk} = \tilde{a}_k^\dagger$$

The operator T is a sesquilinear form of the original operators:

$$T = \sum_{rs} t_{rs} a_r^\dagger a_s$$

It follows that

$$[T, a_s^\dagger] = \sum_{rs'} a_r^\dagger T_{rs'} (\delta_{s's} + S_{s's})$$

and that a matrix relation holds

$$\exp(\mathbf{T} + \mathbf{TS}) = \mathbf{C}$$

A particular transformation of interest is one that creates an orthonormal basis B' so that

$$\mathbf{C}^T (\mathbf{1} + \mathbf{S}) \mathbf{C} = \mathbf{1}$$

It is assumed here that the metric matrix $\mathbf{1} + \mathbf{S}$ is real symmetric and positive definite and that a real transformation \mathbf{C} is considered.

Exercise: Determine the matrix \mathbf{T} for the case that \mathbf{C} is the inverse square root of the metric $\mathbf{1} + \mathbf{S}$.

Mappings of an orthonormal basis, $\mathbf{S} = \mathbf{0}$, onto another orthonormal basis requires an antihermitean matrix \mathbf{T} and if the transformation should be orthogonal \mathbf{T} is antisymmetric. A unitary transformation of operators relating to an orthogonal basis is often given in the form

$$\exp(i\Lambda) : \Lambda = \sum_{rs} \lambda_{rs} a_r^\dagger a_s; \lambda_{rs} = \lambda_{sr}^*$$

The set of all such operators for a basis with M members forms the unitary group $U(M)$. Fock space elements, such as considered above, form basis for irreducible representations of this unitary group.

Exercise: Calculate the effect of the transformation when the operator is

$$\Lambda = -i \frac{\pi}{2} \left[a_r^\dagger a_s - a_s^\dagger a_r \right].$$

Fields and operators:

Fields are entities that take on values at all points in the space one works in. The basis functions of the development can be suppressed through the introduction of field operators:

$$\psi^\dagger(\xi) = \sum_{s,s'=1}^M u_s^\dagger(\xi)(\mathbf{1} + \mathbf{S})_{ss'}^{-1} a_{s'}^\dagger; \quad \psi(\xi) = \sum_{s,s'=1}^M u_s(\xi)(\mathbf{1} + \mathbf{S})_{ss'}^{-1} a_{s'}$$

It is assumed that the overlap \mathbf{S} is self-adjoint. These operators satisfy anticommutation relations as

$$\begin{aligned} [\psi^\dagger(\xi), \psi^\dagger(\xi')]_+ &= 0; \quad [\psi(\xi), \psi(\xi')]_+ = 0; \\ [\psi(\xi), \psi^\dagger(\xi')]_+ &= \sum_{s,s'=1}^M u_s(\xi)(\mathbf{1} + \mathbf{S})_{ss'}^{-1} u_{s'}^\dagger(\xi') \equiv D(\xi; \xi'); \end{aligned}$$

The integral kernel $D(\xi; \xi')$ is a representation of the projector onto the basis space. It will approach a delta-function when the basis becomes complete. Care must be exercised in the derivation of these relations where the multiplication of two component spinors occurs.

Particular products of the field operators are significant. The particle density operator may be expressed, in a symbolic way, for an orthonormal basis as

$$q(\mathbf{r}) = \psi^\dagger(\xi) \circ \psi(\xi) = \sum_{s,s'=1}^M \left[u_{s\alpha}^\dagger(\mathbf{r}) u_{s'\alpha}(\mathbf{r}) + u_{s\beta}^\dagger(\mathbf{r}) u_{s'\beta}(\mathbf{r}) \right] a_s^\dagger a_{s'}$$

A spin density operator is given by the vector field

$$\begin{aligned}
 \mathbf{m}(\mathbf{r}) &= \psi^\dagger(\xi) \circ \begin{pmatrix} \mathbf{e}_z & \mathbf{e}_x - i\mathbf{e}_y \\ \mathbf{e}_x + i\mathbf{e}_y & -\mathbf{e}_z \end{pmatrix} \psi(\xi) \\
 &= \mathbf{e}_z \sum_{s,s'=1}^M \left[u_{s\alpha}^\dagger(\mathbf{r})u_{s'\alpha}(\mathbf{r}) - u_{s\beta}^\dagger(\mathbf{r})u_{s'\beta}(\mathbf{r}) \right] a_s^\dagger a_{s'} \\
 &\quad + \mathbf{e}_x \sum_{s,s'=1}^M \left[u_{s\alpha}^\dagger(\mathbf{r})u_{s'\beta}(\mathbf{r}) + u_{s\beta}^\dagger(\mathbf{r})u_{s'\alpha}(\mathbf{r}) \right] a_s^\dagger a_{s'} \\
 &\quad + \mathbf{e}_y \sum_{s,s'=1}^M \left[-iu_{s\alpha}^\dagger(\mathbf{r})u_{s'\beta}(\mathbf{r}) + iu_{s\beta}^\dagger(\mathbf{r})u_{s'\alpha}(\mathbf{r}) \right] a_s^\dagger a_{s'}
 \end{aligned}$$

The flux or current operator is also a vector field:

$$\begin{aligned}
 \mathbf{j}(\mathbf{r}) &= \frac{1}{2m} \left[\psi^\dagger(\xi) \circ -i\hbar \nabla \psi(\xi) + i\hbar \nabla \psi^\dagger(\xi) \circ \psi(\xi) \right] \\
 &= \frac{-i\hbar}{2m} \sum_{s,s'=1}^M \left[u_{s\alpha}^\dagger(\mathbf{r}) \nabla u_{s'\alpha}(\mathbf{r}) - \nabla u_{s\beta}^\dagger(\mathbf{r}) u_{s'\beta}(\mathbf{r}) \right] a_s^\dagger a_{s'}
 \end{aligned}$$

We define the kinetic energy density operator as the form

$$\begin{aligned}
 K(\mathbf{r}) &= \frac{1}{2m} \left[i\hbar \nabla \psi^\dagger(\xi) \right] \circ \left[-i\hbar \nabla \psi(\xi) \right] \\
 &= \frac{\hbar^2}{2m} \sum_{s,s'=1}^M \left[\nabla u_{s\alpha}^\dagger(\mathbf{r}) \cdot \nabla u_{s'\alpha}(\mathbf{r}) + \nabla u_{s\beta}^\dagger(\mathbf{r}) \cdot \nabla u_{s'\beta}(\mathbf{r}) \right] a_s^\dagger a_{s'}
 \end{aligned}$$

Thus we argue that the hamiltonian for a system of non-interacting electrons subject to the electrostatic potential $\Phi(\mathbf{r})$ is

$$H = \int d\mathbf{r} \left[K(\mathbf{r}) - eq(\mathbf{r})\Phi(\mathbf{r}) \right] = \sum_{s,s'}^{1,M} h_{ss'} a_s^\dagger a_{s'}$$

Magnetic fields will generate terms with spin and current density terms.

Electron interactions.

An electric charge distribution, say $eq(\mathbf{r})$, has a self-energy from the Coulomb force:

$$\begin{aligned}\tilde{H}_{\text{int}} &= \frac{1}{2} \int d\mathbf{r} d\mathbf{r}' \frac{eq(\mathbf{r})eq(\mathbf{r}')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} = \frac{1}{2} \sum_{pqrs}^{1,M} (pq|rs) a_p^\dagger a_q a_r^\dagger a_s \\ &= \frac{1}{2} \sum_{pqrs}^{1,M} (pq|rs) a_p^\dagger a_r^\dagger a_s a_q + \frac{1}{2} \sum_{ps}^{1,M} \left[\sum_{q=1}^M (pq|qs) \right] a_p^\dagger a_s\end{aligned}$$

The basis is orthonormal and the notation for the integrals is

$$(pq|rs) = \int d\mathbf{r} d\mathbf{r}' \frac{e^2 \left[u_{p\alpha}^*(\mathbf{r}) u_{q\alpha}(\mathbf{r}) + u_{p\beta}^*(\mathbf{r}) u_{q\beta}(\mathbf{r}) \right] \left[u_{r\alpha}^*(\mathbf{r}') u_{s\alpha}(\mathbf{r}') + u_{r\beta}^*(\mathbf{r}') u_{s\beta}(\mathbf{r}') \right]}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|}$$

The last of the expressions for the interaction operator above is separated into a one- and a two-electron part. These terms express the fact that the first one annihilates any state with only one particle while the second one can give a non-zero result also on such states. It is considered adequate to disregard the one-electron part since a single electron does not interact with itself in the non-relativistic domain that is considered here.

The neglected term has elements that are expressed in terms of the projector on the basis:

$$\sum_{q=1}^M (pq|qs) = \int d\mathbf{r} d\mathbf{r}' u_p^\dagger(\xi) \circ \frac{e^2 D(\xi; \xi')}{4\pi\epsilon_0|\mathbf{r}-\mathbf{r}'|} \circ u_s(\xi')$$

This form appears as the non-local exchange potential for a system where all spin orbitals in the basis are occupied. Its value depends on the basis and should be eliminated on this ground. A complete basis causes infinities to enter.

The total hamiltonian for an interacting system, within the limitations that the choice of a basis imposes, is thus

$$H = \sum_{rs}^{1,M} h_{rs} a_r^\dagger a_s + \frac{1}{2} \sum_{pqrs}^{1,M} (pq | rs) a_p^\dagger a_r^\dagger a_s a_q$$

It embodies all features of the molecular system through the potential field and the kinetic energy and electrostatic interaction energy of the electrons in the non-relativistic form. No computational simplifications are accomplished, the problem of determining states and energy levels is equally difficult as in the traditional formulation. The form makes it explicit that the choice of a basis and the computation of the matrix elements is a separate problem from the state generation.

Exact eigenstates for this kind of hamiltonian are available only for very simple forms, for instance a linear chain model with a very reduced interaction. Various semiempirical molecular models can be solved accurately by numerical methods since the dimension of the basis and the Fock space is limited.

Accurate energies and states are possible to obtain from the matrix representation of the hamiltonian in a full or truncated set of basis elements from the Fock space. This is known properly as *superposition of configurations* but commonly, very commonly, termed *configuration interaction*, a spectroscopic term. The variational property of this formulation provides a certain measure of control over the error, albeit often useless as a theoretical estimate.

Perturbation theory has always been an alternative to the basic variational method and provides, in conjunction with elements of variational techniques, an option to improve upon an initial attempt. The Møller-Plesset many-body perturbation takes the Hartree-Fock state as the unperturbed, initial state and generates a series for the ground state and its energy. There thus two steps, first one finds an optimal state of the form:

$$|HF\rangle = e^{i\Lambda}|pq\dots n\rangle = |\tilde{p}\tilde{q}\dots\tilde{n}\rangle$$

such that the energy expectation value is stationary:

$$\begin{aligned} 0 &= i\delta\langle HF|H|HF\rangle = \langle pq\dots n|e^{-i\Lambda}[\delta\Lambda, H]e^{i\Lambda}|pq\dots n\rangle \\ &= \langle HF[[\delta\Lambda, H]]HF\rangle \\ &= \sum_{pqr}\left(\delta\lambda_{pr}h_{rq} - h_{pr}\delta\lambda_{rq}\right)\langle HF|a_p^\dagger a_q|HF\rangle \\ &+ \sum_{pqrst}\left\{\delta\lambda_{pt}(tq|rs) - (pt|rs)\delta\lambda_{tq}\right\}\langle HF|a_p^\dagger a_r^\dagger a_s a_q|HF\rangle \end{aligned}$$

The parameters have to be such that unitarity is maintained, $\delta\lambda_{pq} = \delta\lambda_{qp}^*$.

Matrix elements of the operators are expressed in terms density matrix elements,

$$\begin{aligned} \rho_{qp} &= \langle HF|a_p^\dagger a_q|HF\rangle = \delta_{pq} - \langle HF|a_q a_p^\dagger|HF\rangle \\ &= - \begin{vmatrix} 0 & C_{q\tilde{p}} & C_{q\tilde{q}} & \dots & C_{q\tilde{n}} \\ C_{\tilde{p}p}^\dagger & 1 & 0 & \mathbf{0} & 0 \\ C_{\tilde{q}p}^\dagger & 0 & 1 & \mathbf{0} & 0 \\ \vdots & \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ C_{\tilde{n}p}^\dagger & 0 & 0 & \mathbf{0} & 1 \end{vmatrix} = C_{q\tilde{p}}C_{\tilde{p}p}^\dagger + C_{q\tilde{q}}C_{\tilde{q}p}^\dagger + \dots + C_{q\tilde{n}}C_{\tilde{n}p}^\dagger \end{aligned}$$

with

$$C_{q\tilde{p}} = \left[a_q, e^{i\Lambda} a_p^\dagger e^{-i\Lambda} \right]_+; \quad C_{\tilde{p}p}^\dagger = \left[e^{i\Lambda} a_p e^{-i\Lambda}, a_q^\dagger \right]_+$$

These coefficients are the elements of the expansion of the canonical Hartree-Fock orbitals in terms of the original basis.

A similar calculation for the other type of matrix element goes as this:

$$\langle HF | a_p^\dagger a_r^\dagger a_s a_q | HF \rangle$$

$$= \begin{vmatrix} 0 & 0 & C_{s\tilde{p}} & C_{s\tilde{q}} & \cdots & C_{s\tilde{n}} \\ 0 & 0 & C_{q\tilde{p}} & C_{q\tilde{q}} & \cdots & C_{q\tilde{n}} \\ C_{\tilde{p}r}^\dagger & C_{\tilde{p}p}^\dagger & 1 & 0 & \mathbf{0} & 0 \\ C_{\tilde{q}r}^\dagger & C_{\tilde{q}p}^\dagger & 0 & 1 & \mathbf{0} & 0 \\ \vdots & \vdots & \mathbf{0} & \mathbf{0} & \mathbf{1} & \mathbf{0} \\ C_{\tilde{n}r}^\dagger & C_{\tilde{n}p}^\dagger & 0 & 0 & \mathbf{0} & 1 \end{vmatrix} = \rho_{qp}\rho_{sr} - \rho_{qr}\rho_{sp}$$

and the result is the well-known one that the two-particle density matrix elements are antisymmetric direct products of one-particle density matrix elements in Hartree-Fock theory.

Exercise: Derive the result above from the basic anticommutation relations.

The first order variation of the energy expectation value can now be rewritten as

$$\begin{aligned} 0 &= i\delta \langle HF | H | HF \rangle \\ &= \sum_{pqr} \delta\lambda_{pr} (h_{rq}\rho_{qp} - \rho_{rq}h_{qp}) \\ &+ \sum_{pqrst} \delta\lambda_{pr} \left\{ [(rq | ts) - (rs | tq)]\rho_{qp}\rho_{st} - [(qp | ts) - (tp | qs)]\rho_{rq}\rho_{st} \right\} \\ &= \sum_{pqr} \delta\lambda_{pr} (f_{rq}\rho_{qp} - \rho_{rq}f_{qp}) \\ f_{rq} &\equiv h_{rq} + \sum_{st} [(rq | ts) - (rs | tq)]\rho_{st} \end{aligned}$$

Elements of the Fock matrix f are introduced and defined in terms of the density matrix ρ and the two shall commute in order that the expectation is stationary. This leads to the common iterative procedure for the

determination of the canonical Hartree-Fock spin orbitals which diagonalize the hermitean Fock matrix.

Exercise: Derive the formula above in detail by rearranging the sums.

Stability of the Hartree-Fock state.

The self-consistency of the solution to the Hartree-Fock problem tells us that the energy expectation value is stationary for the solution obtained. It is of interest to ascertain the character of this stationary point in Fock space. This requires a calculation of the second variation of the energy expectation value:

$$\begin{aligned}\delta^2 \langle HF | H | HF \rangle &= -\frac{1}{2} \langle HF | [\delta\Lambda, [\delta\Lambda, H]] | HF \rangle \\ &= \frac{1}{2} \sum_{pqrs} \delta\lambda_{pq} \delta\lambda_{rs} A_{pq,rs} \\ A_{pq,rs} &= \langle HF | \left[[a_p^\dagger a_q, H], a_r^\dagger a_s \right] | HF \rangle\end{aligned}$$

The calculations are simplified when the canonical spin orbitals are chosen as the basis, then

$$f_{pq} = \varepsilon_p \delta_{pq}; \rho_{qp} = \rho_p \delta_{pq}; \rho_p \in \{0, 1\}.$$

A normal situation gives a Hartree-Fock state where the occupied spin orbitals with $\rho_p=1$ have lower orbital energies ε_p than unoccupied ones. It is a useful convention to label occupied spin orbitals ℓ, ℓ' , while unoccupied ones are denoted k, k' . We can then conclude that only operators with one occupied and one unoccupied give contributions to the second variation.

It holds that

$$A_{\ell k, k' \ell'} = (\varepsilon_k - \varepsilon_{\ell}) \delta_{kk'} \delta_{\ell \ell'} + (k\ell | \ell' k') - (k k' | \ell' \ell) = A_{\ell' k', k\ell}^*$$

$$A_{k\ell, \ell' k'} = (\varepsilon_k - \varepsilon_{\ell}) \delta_{kk'} \delta_{\ell \ell'} + (k' \ell' | \ell k) - (k' k | \ell \ell') = A_{\ell k, k' \ell'}^*$$

$$A_{\ell k, \ell' k'} = (k\ell | k' \ell') - (k \ell' | k' \ell) = A_{\ell' k', \ell k}$$

$$A_{k\ell, k' \ell'} = (\ell k | \ell' k') - (\ell k' | \ell' k) = A_{\ell k, \ell' k'}^*$$

and the second variation is a hermitean sesquilinear form in the parameters. Its eigenvalues are then real and a stable Hartree-Fock state requires that they are positive. A negative eigenvalue means that there exists an infinitesimal distortion of the Hartree-Fock state which lowers the energy. Spin restricted Hartree-Fock calculations can be stable when distortions are limited but may often be unstable for distortions which change the spin state.

The second variation form plays a role in perturbation analyses. A modification of the one electron part of the hamiltonian induces a change in the Hartree-Fock state and the response is determined in the linear approximation by the inverse of the matrix \mathbf{A} . The resulting relations are known as coupled Hartree-Fock or (linearized) time dependent Hartree-Fock for static and dynamic perturbations respectively.

Many-electron perturbation theory in the temperature domain.

Second quantization is the natural language for the consideration of systems with possible fluctuations in the number of particles. The grand canonical ensemble approach will be used and a general system operator is defined on the Fock space as the exponential

$$\Gamma = \exp[\beta(\Omega - H + \mu N)]$$

Parameters β , Ω , and μ represent the inverse temperature, the free energy, and the chemical potential while $N = \sum_p a_p^\dagger a_p$ is the electron number operator. Normalization provides the relation

$$\Omega = -\frac{1}{\beta} \ln \left\{ \text{Tr} \left[\exp(-\beta H + \beta \mu N) \right] \right\}$$

and the standard forms

$$\langle N \rangle = \text{Tr}(N\Gamma) = -\frac{\partial \Omega}{\partial \mu}; \quad \langle H \rangle = \Omega + \beta \frac{\partial \Omega}{\partial \beta} - \mu \frac{\partial \Omega}{\partial \mu};$$

A system of non-interacting electrons with the hamiltonian

$$H = \sum_p \varepsilon_p a_p^\dagger a_p \equiv F$$

gives the form [Note that $(a_p^\dagger a_p)^2 = a_p^\dagger a_p$]

$$\begin{aligned} \Omega &= -\frac{1}{\beta} \ln \left\{ \text{Tr} \left[\prod_{p=1}^M \exp(\beta(\mu - \varepsilon_p) a_p^\dagger a_p) \right] \right\} \\ &= -\frac{1}{\beta} \sum_{p=1}^M \ln \left\{ \text{Tr} \left[a_p a_p^\dagger + a_p^\dagger a_p e^{\beta(\mu - \varepsilon_p)} \right] \right\} = -\frac{1}{\beta} \sum_{p=1}^M \ln \left\{ 1 + e^{\beta(\mu - \varepsilon_p)} \right\} \end{aligned}$$

and the standard results

$$\langle N \rangle = \sum_{p=1}^M \frac{1}{1 + e^{\beta(\varepsilon_p - \mu)}}; \quad \langle F \rangle = \sum_{p=1}^M \frac{\varepsilon_p}{1 + e^{\beta(\varepsilon_p - \mu)}};$$

The chemical potential μ is also called the Fermi energy, particularly in the theory of solids. Yet another relation is

$$\frac{\partial \Omega}{\partial \varepsilon_p} = \frac{1}{1 + e^{\beta(\varepsilon_p - \mu)}} = \rho_p$$

The spin orbital occupation number is here on the interval [0,1].

Exercise: Show that $\Gamma = \prod_{p=1}^M \left[(1 - \rho_p) a_p a_p^\dagger + \rho_p a_p a_p^\dagger \right]$ for the normalized operator.

A suitable perturbation expansion of the free energy is obtained in powers of the difference between the total hamiltonian and a model hamiltonian for a non-interacting system. Thus we write the system operator in the form

$$\begin{aligned}\Gamma &= \exp[\beta(\Omega + \delta\Omega - H + \mu N)] \\ &= \exp[\beta(\Omega + \delta\Omega - F + \mu N)]\exp(\beta F)\exp(-\beta H)\end{aligned}$$

and observe that F and H do not commute in general but that both commute with the number operator. The shift in the free energy is given by the normalization condition as

$$\begin{aligned}\exp[-\beta\delta\Omega] &= Tr\{\exp[\beta(\Omega - F + \mu N)]\exp(\beta F)\exp(-\beta H)\} \\ &= \langle \exp(\beta F)\exp(-\beta H) \rangle\end{aligned}$$

where the average value is taken over the unperturbed ensemble defined from the F -operator.

We consider the operator in the average value above and obtain the integral equation

$$\begin{aligned}\exp(\beta F)\exp(-\beta H) &\equiv S(\beta) \\ &= S(0) + \int_0^\beta d\tau \frac{dS(\tau)}{d\tau} = S(0) - \int_0^\beta d\tau V(\tau)S(\tau) \\ V(\tau) &= e^{\tau F}(H - F)e^{-\tau F}\end{aligned}$$

The similarity transformation affects the individual operators in the hamiltonian,

$$\begin{aligned}e^{\tau F} a_p^\dagger e^{-\tau F} &= \exp(\tau \varepsilon_p a_p^\dagger a_p) a_p^\dagger \exp(-\tau \varepsilon_p a_p^\dagger a_p) = \exp(\tau \varepsilon_p) a_p^\dagger \equiv a_p^\dagger(\tau) \\ e^{\tau F} a_p e^{-\tau F} &= \exp(\tau \varepsilon_p a_p^\dagger a_p) a_p \exp(-\tau \varepsilon_p a_p^\dagger a_p) = \exp(-\tau \varepsilon_p) a_p \equiv a_p(\tau)\end{aligned}$$

The notation of hermitean conjugation will be kept although it cannot be used as normally implied.

Energy perturbations are then calculated from the expression

$$\begin{aligned} \exp[-\beta\delta\Omega] &= \langle S(\beta) \rangle = 1 - \int_0^\beta d\tau \langle V(\tau) S(\tau) \rangle \\ &= 1 - \int_0^\beta d\tau \langle V(\tau) \rangle + \int_0^\beta d\tau \int_0^\tau d\tau' \langle V(\tau) V(\tau') \rangle - \dots \end{aligned}$$

and the iterated form to arbitrary order. The concept of "time ordering" is introduced and implies that operators always shall be ordered with decreasing "time"-argument τ from left to right under the integral signs.

Then one writes

$$\int_0^\beta d\tau \int_0^\tau d\tau' \langle V(\tau) V(\tau') \rangle = \frac{1}{2} \int_0^\beta d\tau \int_0^\beta d\tau' \langle T[V(\tau) V(\tau')] \rangle$$

and corresponding expressions for the higher order terms.

Evaluation of the first order term proceeds as follows:

$$\begin{aligned} \langle V(\tau) \rangle &= \langle H - F \rangle \\ &= \sum_{pq} (h_{pq} - \varepsilon_p \delta_{pq}) \langle a_p^\dagger a_q \rangle + \frac{1}{2} \sum_{pqrs} (pq | rs) \langle a_p^\dagger a_r^\dagger a_s a_q \rangle \\ &= \sum_p (h_{pp} - \varepsilon_p) \rho_p + \frac{1}{2} \sum_{pr} [(pp | rr) - (pr | rp)] \rho_p \rho_r \\ &= -\frac{1}{2} \sum_{pr} [(pp | rr) - (pr | rp)] \rho_p \rho_r \end{aligned}$$

The last equality holds when the unperturbed operator F is a generalized Hartree-Fock operator with non-integral occupation numbers, sometimes called the grand canonical Hartree-Fock. We recognize then that the first order perturbation energy equals the *negative* of the electron interaction energy in the Hartree-Fock ensemble since the sum of orbital energies includes the mutual interactions twice.

The second order contribution to the expansion requires the determination of average values of products of up to eight elementary creation and annihilation operators. This proceeds by rearrangement of the operators in the fashion used for the calculation of the metric matrix in Fock space. The new thing is that the unperturbed system operator takes the role of the vacuum state and that operator products under the trace operation can be cyclically moved without an effect on the result. Thus

$$\begin{aligned} a_p^\dagger(\tau) \exp[\beta(\Omega - F + \mu N)] &= \exp[\beta(\Omega - F + \mu N)] a_p^\dagger(\tau) (1 - \rho_p) \\ a_p(\tau) \exp[\beta(\Omega - F + \mu N)] &= \exp[\beta(\Omega - F + \mu N)] a_p(\tau) \rho_p \end{aligned}$$

so that

$$\begin{aligned} \langle T[a_p(\tau) a_q^\dagger(\tau')] \rangle &= -\langle T[a_q^\dagger(\tau') a_p(\tau)] \rangle \\ &= \Theta(\tau - \tau') \langle a_p(\tau) a_q^\dagger(\tau') \rangle - \Theta(\tau' - \tau) \langle a_q^\dagger(\tau') a_p(\tau) \rangle \\ &= \delta_{pq} \exp[\varepsilon_p(\tau' - \tau)] \left\{ (1 - \rho_p) \Theta(\tau - \tau') - \rho_p \Theta(\tau' - \tau) \right\} \equiv g(p\tau, q\tau') \end{aligned}$$

a result which follows readily from the form of the exercise above. The term contraction is occasionally used for a form like this, it will be termed a propagator here since it is closely related to the time-dependent form.

Induction can be used to derive the general result for the average value of a "time" ordered product of operators:

$$\begin{aligned} &\langle T[a_n(\tau_n) \dots a_q(\tau_2) a_p(\tau_1) a_{p'}^\dagger(\tau'_1) a_{q'}^\dagger(\tau'_2) \dots a_{n'}^\dagger(\tau'_n)] \rangle \\ &= \begin{vmatrix} g(p\tau_1, p'\tau'_1) & g(p\tau_1, q'\tau'_2) & \dots & g(p\tau_1, n'\tau'_n) \\ g(q\tau_2, p'\tau'_1) & g(q\tau_2, q'\tau'_2) & \dots & g(q\tau_2, n'\tau'_n) \\ \vdots & \vdots & \ddots & \vdots \\ g(n\tau_n, p'\tau'_1) & g(n\tau_n, q'\tau'_2) & \dots & g(n\tau_n, n'\tau'_n) \end{vmatrix} \end{aligned}$$

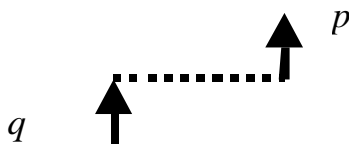
This result is called Wick's theorem and was first derived in quantum electrodynamics. The Kronecker delta in the definition of the propagator is seen to imply that there should be a "perfect pairing" between creation and annihilation operators.

The second order term in our expansion has the integrand as the more explicit form

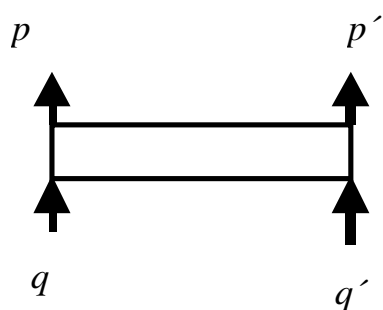
$$\begin{aligned} \langle T[V(\tau)V(\tau')] \rangle &= \sum_{pqrs} (h_{pq} - \varepsilon_p \delta_{pq}) (h_{rs} - \varepsilon_r \delta_{rs}) \langle T[a_p^\dagger(\tau)a_q(\tau)a_r^\dagger(\tau')a_s(\tau')] \rangle \\ &+ \frac{1}{2} \sum_{pqrsr's'} (h_{pq} - \varepsilon_p \delta_{pq}) (rs | r's') \langle T[a_p^\dagger(\tau)a_q(\tau)a_r^\dagger(\tau')a_{r'}^\dagger(\tau')a_{s'}(\tau')a_s(\tau')] \rangle \\ &+ \frac{1}{2} \sum_{pp'q'rs} (pq | p'q') (h_{rs} - \varepsilon_r \delta_{rs}) \langle T[a_p^\dagger(\tau)a_{p'}^\dagger(\tau)a_{q'}(\tau)a_q(\tau)a_r^\dagger(\tau')a_s(\tau')] \rangle \\ &+ \frac{1}{4} \sum_{pp'q'rsr's'} (pq | p'q') (rs | r's') \langle T[a_p^\dagger(\tau)a_{p'}^\dagger(\tau)a_{q'}(\tau)a_q(\tau)a_r^\dagger(\tau')a_{r'}^\dagger(\tau')a_{s'}(\tau')a_s(\tau')] \rangle \end{aligned}$$

which appears somewhat awkward.

The concept of a diagrammatic representation simplifies this quite considerably. Each term from the one electron part is associated with one creation and one annihilation operator, it appears as a "scattering" of an electron from spin orbital q to spin orbital p . A Feynman type representation of this is the diagram

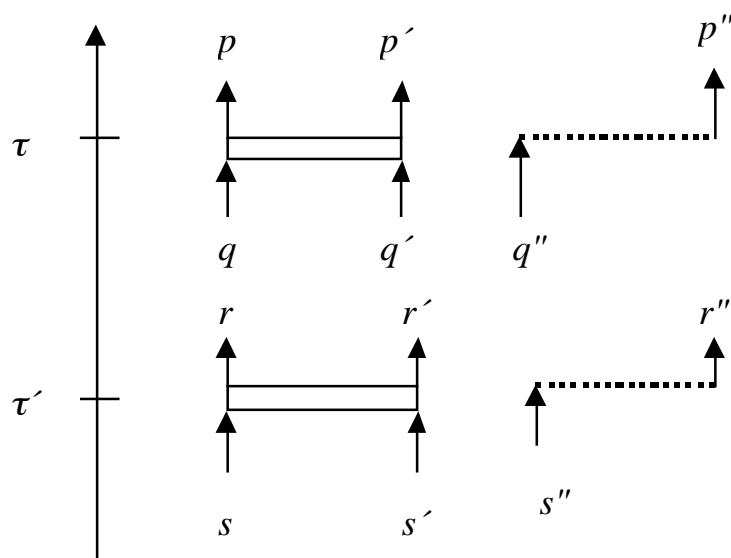


Similarly, a two electron term "scatters" a pair of spin orbitals into another pair, and the diagram is



Electron interaction diagrams are often drawn as a single line since the Coulomb interaction acts between two points. The spin orbital notation indicates the possibility for a more general interaction.

The analysis of the second order term has shown that there is a one and a two electron contribution at both "times". Thus we draw a picture representing this as

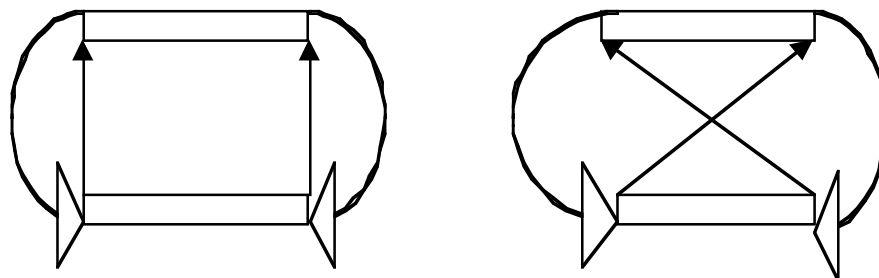


The elements of this diagram are then to be combined with the possibilities for the averages of "time" ordered products. This means that an arrow exiting from a point has to end at another point in the diagram and that no open ends occur. The result is classified in two separate sets, one that does not connect an element at τ with one at τ' and another that does. The former will represent the product

$$\langle V(\tau) \rangle \langle V(\tau') \rangle = \langle V(0) \rangle^2$$

and is already calculated. The second set connects an element at τ with one at τ' and involves propagators. A proper Hartree-Fock ensemble has then the property that all diagrams that has one electron part is cancelled by other diagrams where two electron parts are joined by only one pair of propagators. This will not be proven here.

The end result for the second order perturbation contribution is represented by the two diagrams



[Note: I could not figure out how to get smaller arrowheads on the curved ones in the Word picture editing section.]

Spin orbital indices have been dropped since they are to be summed over and the symmetry of the interaction integrals gives an equivalence between corresponding, e. g. topologically similar diagrams. There are four propagator lines in these diagrams that depend on the "time" difference. Two go forward in "time" while two go backwards. The Feynman picture considers this as two particles and two holes moving forward. The temperature formulation does not make a clear separation between occupied or hole states and unoccupied or particle states except in the limit of zero temperature.

Detailed analysis of the symmetry options leads to the final form for the relevant second order contribution:

$$\begin{aligned}
 & \frac{1}{2} \int_0^\beta d\tau \int_0^\beta d\tau' \langle T[V(\tau)V(\tau')] \rangle \\
 &= \frac{1}{4} \sum_{pqrs} (pq | rs) [(qp | sr) - (sp | qr)] \\
 & \quad \times \int_0^\beta d\tau \int_0^\beta d\tau' g(p\tau, p\tau') g(q\tau', q\tau) g(r\tau, r\tau') g(s\tau', s\tau) \\
 &= \frac{\beta}{4} \sum_{pqrs} (pq | rs) [(qp | sr) - (sp | qr)] \frac{(1-\rho_p)\rho_q(1-\rho_r)\rho_s - \rho_p(1-\rho_q)\rho_r(1-\rho_s)}{\varepsilon_p - \varepsilon_q + \varepsilon_r - \varepsilon_s} \\
 &= \frac{\beta}{4} \sum_{pqrs} |(pq | rs) - (ps | rq)|^2 \frac{(1-\rho_p)\rho_q(1-\rho_r)\rho_s}{\varepsilon_p - \varepsilon_q + \varepsilon_r - \varepsilon_s}
 \end{aligned}$$

Exercise: Check the integrals!

The expression is identical to the Møller-Plesset form in the zero temperature limit where occupation numbers are zero or one.

Contributions of higher order are classified in terms of connected or linked diagrams and the rules for the expressions are derived in several texts. It was seen here that the form for $\delta\Omega$ includes only linked diagrams through second order and the general statement holds to any order.

Clusters and their couplings.

Perturbation expansions are not generally guaranteed to converge and the radius of convergence, if it exists, is difficult to determine. Thus there has been a search for alternative methods where certain terms in the perturbation series can be summed to infinite order through a another form of series expansion. One such technique is currently popular and the

subject of intense development, it is termed the Coupled Cluster method and comes in various guises.

The basic observation is that a linear combination of N -electron states is generated from the Hartree-Fock state by the operation

$$e^T |HF\rangle = \exp\left(\sum_{k\ell} t_\ell^k a_k^\dagger a_\ell\right) |HF\rangle$$

$$= |HF\rangle + \sum_{k\ell} a_k^\dagger a_\ell |HF\rangle t_\ell^k + \frac{1}{2} \sum_{k\ell k'\ell'} a_k^\dagger a_{k'}^\dagger a_{\ell'} a_\ell |HF\rangle t_\ell^k t_{\ell'}^{k'} + \dots$$

The notation from above about occupied, ℓ , and unoccupied, k , spin orbitals is used here. The new state is a non-linear expression in the parameters t_ℓ^k and may possibly be determined so as to improve the Hartree-Fock state. A stable such state will not be interacting with the states where single substitutions of an occupied with an unoccupied spin orbital has taken place and little improvement is expected from this form.

More general T -operators include the simultaneous replacements of n occupied with n unoccupied spin orbitals,

$$T = \sum_{k\ell} t_\ell^k a_k^\dagger a_\ell + \sum_{k\ell k'\ell'} t_{\ell\ell'}^{kk'} a_k^\dagger a_{k'}^\dagger a_{\ell'} a_\ell + \dots$$

It should be noted that then it holds that

$$e^T |HF\rangle = |HF\rangle + \sum_{k\ell} a_k^\dagger a_\ell |HF\rangle t_\ell^k + \sum_{k\ell k'\ell'} a_k^\dagger a_{k'}^\dagger a_{\ell'} a_\ell |HF\rangle \left(\frac{1}{2} t_\ell^k t_{\ell'}^{k'} + t_{\ell\ell'}^{kk'}\right) + \dots$$

and that in general any state can be generated by such an operator.

The dimension of the N -electron space in the Fock space is $\binom{M}{N}$ and each state requires that number of amplitudes to be defined. There are $N(M-N)$ coefficients t_ℓ^k and $\frac{1}{4}N(N-1)(M-N)(M-N-1)$ of the type $t_{\ell\ell'}^{kk'}$. Accordingly

there are fewer numbers to calculate for a low order T than in the full space expansion and experience has shown that accurate results can be obtained with modest orders of substitution operators in the T form.

Calculation of the parameters could possibly be done through the conventional variational method but the forms get quite awkward. The preferred procedure is to abandon the variational features of a state and to examine the operator equation representing the Schrödinger equation:

$$(E - H)e^T |HF\rangle = 0$$

and the related form

$$e^{-T}(E - H)e^T |HF\rangle = \left(E - H + [T, H] - \frac{1}{2}[T, [T, H]] + \dots \right) |HF\rangle = 0$$

It has been proven and might be seen by inspection that regardless of the order of the T , the nested commutator series ends after the fourth order term. Thus there remains to project the left hand side onto the manifold of N particle states and to solve for the parameters. Once they are known one calculates the energy as

$$E = \langle HF | H - [T, H] + \frac{1}{2}[T, [T, H]] - \dots | HF \rangle$$

Cluster operators T are given that name in correspondence to similar expansions in the theory of gases. So called doubles clusters couple two particle-hole pairs while higher order operators bring in couplings between several such pairs.

A prominent feature of the coupled cluster energy is the so called size consistency. The exponential form generates the simultaneous correlation corrections to pairs that are not properly included in the perturbation approach until it reaches infinite order.