Many Electron Theory:

Time dependent perturbations and propagation.

Continued notes for a workgroup September-October 2002.

Notes prepared by Jan Linderberg, September 2002

Hamiltonians with time dependence.

Evolution in time is governed by the hamiltonian of the system and when there is an explicit dependence upon time in the hamiltonian it is no longer possible to separate state vectors into a product of a time dependent phase factor and a stationary eigenstate of a time independent hamiltonian. Spectroscopy is built on the premise that absorption and emission occurs between such states and that a low order perturbation treatment suffices for the description of such processes. Molecular scattering processes and reaction dynamics is not well suited for such a treatment and requires more detailed analysis and somewhat different approximation methods.

Variational formulations are useful both for spectroscopic and dynamical problems. The Schrödinger equation obtains from the condition, attributed to Frenkel,

$$\delta\left[\frac{1}{2}\left\langle i\hbar\frac{\partial\Psi}{\partial t}\middle|\Psi\right\rangle + \frac{1}{2}\left\langle\Psi\middle|i\hbar\frac{\partial\Psi}{\partial t}\right\rangle - \left\langle\Psi|H(t)|\Psi\right\rangle\right] = 0$$

and is a first order differential equation in time. It needs a starting value for the state and is used to propagate this state towards later times, or, occasionally, to previous ones. This is different from the time independent variational form which leads to a second order partial differential equation and certain boundary conditions.

Many electron theory in the perturbation form for a time independent hamiltonian was developed from an *adiabatic hypothesis* that the electron interaction could be considered time dependent and vanishing infinitely long ago. Convergence of this procedure has been questioned.

Dirac considered the time evolution of the density matrix in the Hartree-Fock approximation, that is the state vector should at any time be of the Slater determinant form with time dependent spin orbitals. Then one calculates the value of the lagrangian

$$L(t) = \tfrac{1}{2}\left\langle i\hbar\tfrac{\partial\Psi}{\partial t}\middle|\Psi\right\rangle + \tfrac{1}{2}\left\langle\Psi\middle|i\hbar\tfrac{\partial\Psi}{\partial t}\right\rangle - \left\langle\Psi|H(t)|\Psi\right\rangle$$

for a state

$$|THF\rangle = e^{i\Lambda(t)}|pq\ldots n\rangle$$

The last term in the lagrangian comes out as in the normal Hartree-Fock calculation with consideration that the density matrix now depends on time. It holds that

$$i\hbar\tfrac{\partial}{\partial t}|THF\rangle = -\hbar\dot{\Lambda}(t)e^{i\Lambda(t)}|pq\ldots n\rangle = -\hbar\dot{\Lambda}(t)|THF\rangle$$

so that

$$L(t) = -\hbar\sum_{rs}\dot{\lambda}_{rs}(t)\rho_{sr}(t) - \sum_{rs}h_{rs}(t)\rho_{sr}(t)$$
$$-\tfrac{1}{2}\sum_{pqrs}\left[(pq\,|rs) - (ps\,|rq)\right]\rho_{qp}(t)\rho_{sr}(t)$$

This expression simplifies when the canonical spin orbitals are used and becomes

$$L(t) = -\hbar\sum_{\ell}\dot{\lambda}_{\ell}(t) - \sum_{\ell}\varepsilon_{\ell}(t) + \tfrac{1}{2}\sum_{\ell\ell'}\left[(\ell\ell\,|\,\ell'\ell') - (\ell\ell'\,|\,\ell'\ell)\right]$$

which has the value zero when the sum of the λ´s is a linear function of time with the slope being the negative of the Hartree-Fock energy expectation value.

A small deformation of the Hartree-Fock state should not change the value of the lagrangian when a stationary solution is found. We use

$$|THF\rangle \Rightarrow |THF\rangle + i\delta\Lambda(t)|THF\rangle$$

$$i\hbar \tfrac{\partial}{\partial t}|THF\rangle \Rightarrow -\hbar\dot{\Lambda}(t)|THF\rangle - \hbar\delta\dot{\Lambda}(t)|THF\rangle - i\hbar\dot{\Lambda}(t)\delta\Lambda(t)|THF\rangle$$

and obtain

$$\delta\langle THF|i\hbar \tfrac{\partial}{\partial t}|THF\rangle =$$

$$-\hbar\langle THF|\delta\dot{\Lambda}(t)|THF\rangle - i\hbar\langle THF\left[\delta\Lambda(t),\dot{\Lambda}(t)\right]THF\rangle =$$

$$-\hbar\sum_{rs}\delta\dot{\lambda}_{rs}(t)\rho_{sr}(t) - i\hbar\sum_{prs}\delta\lambda_{rs}(t)\left[\dot{\lambda}_{sp}(t)\rho_{pr}(t) - \rho_{sp}(t)\dot{\lambda}_{pr}(t)\right] =$$

$$-\hbar\sum_{rs}\delta\dot{\lambda}_{rs}(t)\rho_{sr}(t) - \hbar\sum_{rs}\delta\lambda_{rs}(t)\dot{\rho}_{sr}(t)$$

The previous result for the variation of the Hartree-Fock energy expectation value gives

$$\delta L(t) = -\hbar\sum_{rs}\delta\dot{\lambda}_{rs}(t)\rho_{sr}(t)$$

$$-\sum_{rs}\delta\lambda_{rs}(t)\left\{\hbar\dot{\rho}_{sr}(t) + i\sum_{p}\left[f_{sp}(t)\rho_{pr}(t) - \rho_{sp}(t)f_{pr}(t)\right]\right\}$$

and the condition for arbitrary variations is

$$\hbar\dot{\rho}_{sr}(t) + i\sum_{p}\left[f_{sp}(t)\rho_{pr}(t) - \rho_{sp}(t)f_{pr}(t)\right] = 0$$

A matrix form of this equation is

$$i\hbar\dot{\rho}(t) = \left[\mathbf{f}(t),\rho(t)\right]$$

which shows that the density matrix transforms inversely to the equation of motion for a Heisenberg operator.

A proper Hartree-Fock density matrix is a projection operator onto the occupied set of spin orbitals and the first term of the variation of the lagrangian vanishes when the time derivative of the deformation generator has no components in this space.

The time dependent Hartree-Fock equations have found use in collision problems, molecular as well as nuclear. Our emphasis will be on the

spectroscopy of electronic systems. We consider the effect of an external field with some dependence on time,

$$h_{rs}(t) = h_{rs} + v_{rs}(t)$$

and a density matrix with a small deviation from a stationary state,

$$\rho_{sr}(t) = \delta_{sr}n_s + \delta\rho_{sr}(t)$$

The basis is taken as the canonical one for the stationary state. The elements of the Fock matrix are then

$$f_{rs}(t) = \delta_{rs}\varepsilon_s + v_{rs}(t) + \sum_{pq}\left[(rs\,|\,pq) - (rq\,|\,ps)\right]\delta\rho_{qp}(t)$$

These forms are inserted into the equation of motion for the density matrix and terms of second and higher order in the perturbations are discarded to obtain the *linearized time-dependent Hartree-Fock equations:*

$$\hbar\delta\dot{\rho}_{sr}(t) + iv_{sr}(t)\left[n_r - n_s\right] + i\left[\varepsilon_s - \varepsilon_r\right]\delta\rho_{sr}(t)$$
$$+i\left[n_r - n_s\right]\sum_{pq}\left[(sr\,|\,pq) - (sq\,|\,pr)\right]\delta\rho_{qp}(t) = 0$$

Were we to neglect the terms that depend explicitly on the electron interactions, then a direct integration gives

$$\delta\rho_{sr}(t) = \delta\rho_{sr}(0) + \tfrac{i}{\hbar}\left[n_s - n_r\right]\int_0^t dt' v_{sr}(t')\exp\left[\tfrac{i}{\hbar}(t' - t)(\varepsilon_s - \varepsilon_r)\right]$$

Resonance occurs when the perturbation has a frequency component that equals the spin orbital energy difference.

Fourier analysis transforms the differential equations above to algebraic ones. We introduce the notation ℓ to indicate occupied spin orbitals and k to refer to unoccupied ones. Thus

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$$\hbar\omega\delta\tilde{\rho}_{k\ell}(\omega) + \tilde{v}_{k\ell}(\omega) + \left[\varepsilon_k - \varepsilon_\ell\right]\delta\tilde{\rho}_{k\ell}(\omega)$$

$$+\sum_{pq}\left[(k\ell \mid \ell'k') - (kk' \mid \ell'\ell)\right]\delta\tilde{\rho}_{k'\ell'}(\omega)$$

$$+\sum_{pq}\left[(k\ell \mid k'\ell') - (k\ell' \mid k'\ell)\right]\delta\tilde{\rho}_{\ell'k'}(\omega) = 0$$

$$\hbar\omega\delta\tilde{\rho}_{\ell k}(\omega) - \tilde{v}_{\ell k}(\omega) - \left[\varepsilon_k - \varepsilon_\ell\right]\delta\tilde{\rho}_{\ell k}(\omega)$$

$$-\sum_{k'\ell'}\left[(\ell k \mid \ell'k') - (\ell k' \mid \ell'k)\right]\delta\tilde{\rho}_{k'\ell'}(\omega)$$

$$-\sum_{k'\ell'}\left[(\ell k \mid k'\ell') - (\ell\ell' \mid k'k)\right]\delta\tilde{\rho}_{\ell'k'}(\omega) = 0$$

The matrix elements that occur in these equations are the same as those considered in the stability analysis of the Hartree-Fock state. It is convenient to order the elements of the perturbed density matrix as a one-dimensional array. We introduce to this end an index σ to indicate a pair $(k\ell)$ and use $-\sigma$ for the pair (ℓk). Then it holds that

$$\hbar\omega\delta\tilde{\rho}_\sigma + \tilde{v}_\sigma + \sum_{\sigma'}\left(A_{\sigma,\sigma'}\delta\tilde{\rho}_{\sigma'} + A_{\sigma,-\sigma'}\delta\tilde{\rho}_{-\sigma'}\right) = 0;$$

$$-\hbar\omega\delta\tilde{\rho}_{-\sigma} + \tilde{v}_{-\sigma} + \sum_{\sigma'}\left(A_{-\sigma,\sigma'}\delta\tilde{\rho}_{\sigma'} + A_{-\sigma,-\sigma'}\delta\tilde{\rho}_{-\sigma'}\right) = 0$$

which is a linear equation system for the perturbed density matrix elements. A perturbation, which is constant in time, gives a deformation of the Hartree-Fock state from these *coupled equations* provided the state is stable.

Singularities are to be anticipated in the equation system above for certain frequencies ω. Such frequencies are interpreted as excitation frequencies of the system. We saw above that neglect of electron interactions, beyond what is included in the Fock matrix, gives the Bohr frequency rules.

A positive definite matrix **A** has a Cholesky decomposition such that

$$\mathbf{A} = \mathbf{L}\mathbf{L}^\dagger; \quad A_{\pm\sigma,\pm\sigma'} = \sum_\tau L_{\pm\sigma,\tau}L^*_{\pm\sigma',\tau}$$

and we define new quantities as

$$\delta\rho_\tau = \sum_\sigma \left(L^*_{\sigma,\tau}\delta\rho_\sigma + L^*_{-\sigma,\tau}\delta\rho_{-\sigma} \right)$$

The inverse relation is denoted

$$\delta\rho_{\pm\sigma} = \sum_\tau L^{-*}_{\tau,\pm\sigma}\delta\rho_\tau .$$

A somewhat shortened notation is used for the complex conjugates of the elements of the inverse to the matrix **L**.

The transformed elements of the density matrix satisfy the equation system

$$\delta\rho_\tau + \hbar\omega\sum_{\tau'}\Theta_{\tau,\tau'}\delta\rho_{\tau'} + \sum_\sigma\left(L^{-1}_{\tau,\sigma}v_\sigma + L^{-1}_{\tau,-\sigma}v_{-\sigma} \right) = 0$$

$$\Theta_{\tau,\tau'} = \sum_\sigma\left(L^{-1}_{\tau,\sigma}L^{-*}_{\tau',\sigma} - L^{-1}_{\tau,-\sigma}L^{-*}_{\tau',-\sigma} \right)$$

It follows from the construction that Θ is an hermitean matrix and it can be shown that its eigenvalues are occurring in pairs of opposite sign. Real spin orbitals and matrix elements provide for some simplifications in the actual calculation of these matrices.

The solution of the equation system offers the possibility to calculate the perturbed expectation value of an operator. Such an operator may be the dipole operator with the form

$$D = \sum_{rs} d_{rs}a_r^\dagger a_s$$

so that

$$\langle D\rangle = \sum_{rs}d_{rs}\rho_{sr} = \sum_\ell d_{\ell\ell} + \sum_\sigma\left(d_{\ell k}\delta\rho_\sigma + d_{k\ell}\delta\rho_{-\sigma} \right)$$

There should also be integration over the frequencies from the Fourier transformation. A perturbation with a simple harmonic time dependence gives an induced dipole moment with the same frequency and the proportionality between the induce dipole and the field strength is

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expressed in terms of a polarizability that can be calculated from the equation system.

Almost every electronic structure calculation involves a spin independent hamiltonian and the Hartree-Fock orbitals are normally spin degenerate and may be characterized as either $\alpha-$ or $\beta-$orbitals. A singlet ground state admits single excitations only to another singlet or to a three-fold degenerate triplet level. Accordingly one can separate the density matrix distortion elements into singlet and triplet components. The matrix problem separates into four independent ones, three of which are identical and refer to triplet excitations. Point group symmetry simplifies the solution further when present. The perturbation from an electric field can be expressed either in the dipole length form or in the dipole velocity form. Time dependent linearized Hartree-Fock maintains the equivalence between the two formulations provided that dipole velocity operator representation satisfies the fundamental relation

$$\dot{D} = \tfrac{i}{\hbar}\left[D, H\right]$$

This holds in a complete basis and may be reasonably accurate in a large basis for the relevant matrix elements. Some model hamiltonians are constructed so as to offer this relation.