Derivation of Time Dependent Hartree-Fock (TDHF) Equations

Joshua Goings

Department of Chemistry, University of Washington

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We start with the time-dependent Schrödinger equation, given in Hartree-Fock form, along with its adjoint:

$$i\frac{\partial}{\partial t}\mathbf{C} = \mathbf{F}\mathbf{C}$$

$$-i\frac{\partial}{\partial t}\mathbf{C}^\dagger = \mathbf{C}^\dagger\mathbf{F} \tag{1}$$

with $\mathbf{C}$ as the matrix of coefficients for the Hartree Fock eigenvalue equation and $\mathbf{F}$ is the Fock matrix, which is Hermitian. Now,

$$i\frac{\partial}{\partial t}\mathbf{C}\mathbf{C}^\dagger = i\left(\frac{\partial}{\partial t}\mathbf{C}\mathbf{C}^\dagger + \mathbf{C}\frac{\partial}{\partial t}\mathbf{C}^\dagger\right)$$

$$\tag{2}$$

Substituting the first two expressions into the right hand side, these two expressions yields the Dirac form of the time-dependent Hartree-Fock equations,

$$i\frac{\partial}{\partial t}\mathbf{C}\mathbf{C}^\dagger = i\frac{\partial}{\partial t}\mathbf{P} = i\left(-i\mathbf{F}\mathbf{C}\mathbf{C}^\dagger + i\mathbf{C}\mathbf{C}^\dagger\mathbf{F}\right)$$

$$\tag{3}$$

where $\mathbf{F}$ is the Fock matrix and $\mathbf{P} = \mathbf{C}\mathbf{C}^\dagger$ is the density matrix, same as in the time independent Hartree-Fock equations. Before a time dependent perturbation is applied, we assume that the system is in its electronic ground state, such that

$$\mathbf{F}^{(0)}\mathbf{P}^{(0)} - \mathbf{P}^{(0)}\mathbf{F}^{(0)} = 0 \tag{4}$$

and

$$\mathbf{P}^{(0)}\mathbf{P}^{(0)} = \mathbf{P}^{(0)} \tag{5}$$

with $\mathbf{P}^{(0)}$ and $\mathbf{F}^{(0)}$ as the unperturbed density and Fock matrix, respectively. The first condition comes from the fact that commuting matrices share a common set of eigenvectors, and the second comes from the fact that at convergence

the eigenvectors of the Fock matrix are orthonormal. (Recall that the density matrix may be written as $\mathbf{P} = \mathbf{CC}^\dagger$, where the columns of $\mathbf{C}$ form an orthonormal set, e.g. $\mathbf{C}^\dagger\mathbf{C} = \mathbf{1}$). The Fock matrix elements are given by

$$F_{pq}^{(0)} = H_{pq}^{core} + \sum_{rs} P_{rs}[(pq|sr) - (pr|sq)] \tag{6}$$

Note the Fock matrix dependence on the density matrix. At convergence, the Fock matrix is diagonal, with the elements corresponding to the orbital energies ϵ.

$$F_{pq}^{(0)} = \delta_{pq}\epsilon_p \tag{7}$$

Furthermore, the density matrix enjoys the following relations:

$$P_{ij}^{(0)} = \delta_{ij} \qquad\qquad P_{ia}^{(0)} = P_{ai}^{(0)} = P_{ab}^{(0)} = 0 \tag{8}$$

Following convention, indices $\{i, j, ...\}$ correspond to occupied orbitals, $\{a, b, ...\}$ correspond to unoccupied orbitals, and $\{p, q, ...\}$ correspond to general orbitals. In general perturbation theory, a perturbed wavefunction (or density matrix, for our purposes) can be decomposed, to first order, as

$$\mathbf{P} = \mathbf{P}^{(0)} + \mathbf{P}^{(1)} \tag{9}$$

and likewise for the density-dependent Fock matrix

$$\mathbf{F} = \mathbf{F}^{(0)} + \mathbf{F}^{(1)} \tag{10}$$

where the superscript (1) indicates the first-order time dependent change. Inserting the expressions 9 and 10 into the time-dependent equation 3 and collecting only the first order terms yields

$$\mathbf{F}^{(0)}\mathbf{P}^{(1)} - \mathbf{P}^{(1)}\mathbf{F}^{(0)} + \mathbf{F}^{(1)}\mathbf{P}^{(0)} - \mathbf{P}^{(0)}\mathbf{F}^{(1)} = i\frac{\partial}{\partial t}\mathbf{P}^{(1)} \tag{11}$$

The time-dependent perturbation can be described by a single Fourier component,

$$g_{pq} = \frac{1}{2}[f_{pq}e^{-i\omega t} + f_{qp}^* e^{i\omega t}] \tag{12}$$

The matrix f is a one-electron operator, which describes the applied perturbation. This perturbation acts on the electron density, resulting in a first order Fock matrix response

$$\Delta F_{pq}^{(0)} = \sum_{st} \frac{\partial F_{pq}^{(0)}}{\partial P_{st}} P_{st}^{(1)} \tag{13}$$

so that the overall first order change in the Fock matrix is

$$F_{pq}^{(1)} = g_{pq} + \Delta F_{pq}^{(0)} \tag{14}$$

Similarly, the first order density response is given as

$$P_{pq}^{(1)} = \frac{1}{2}[d_{pq}e^{-i\omega t} + d_{qp}^* e^{i\omega t}] \tag{15}$$

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with d_{pq} as the perturbation densities. Plugging the above expressions for $\mathbf{F}^{(1)}$ and $\mathbf{P}^{(1)}$ into the first order TDHF equation 11, and collecting the terms containing $e^{-i\omega t}$ gives (after some algebra):

$$\sum_q F_{pq}^{(0)} d_{qr} - d_{pq} F_{qr}^{(0)} + \left(f_{pq} + \sum_{st} \frac{\partial F_{pq}^{(0)}}{\partial P_{st}} d_{st} \right) P_{qr}^{(0)} -$$

$$P_{pq}^{(0)} \left(f_{qr} + \sum_{st} \frac{\partial F_{qr}^{(0)}}{\partial P_{st}} d_{st} \right) = \omega d_{pr} \quad (16)$$

The terms multiplied by $e^{i\omega t}$ give the complex conjugate of the above expression. Because the density matrix must be idempotent, we can show that

$$\sum_q \{ P_{pq}^{(0)} P_{qr}^{(1)} + P_{pq}^{(1)} P_{qr}^{(0)} \} = P_{pr}^{(1)} \quad (17)$$

If $\mathbf{PP} = \mathbf{P}$, and we expand $\mathbf{P}$ as a perturbation with arbitrary scalar λ, we have:

$$(\mathbf{P}^{(0)} + \lambda \mathbf{P}^{(1)} + \lambda^2 \mathbf{P}^{(2)} + \dots)(\mathbf{P}^{(0)} + \lambda \mathbf{P}^{(1)} + \lambda^2 \mathbf{P}^{(2)} + \dots)$$

$$= (\mathbf{P}^{(0)} + \lambda \mathbf{P}^{(1)} + \lambda^2 \mathbf{P}^{(2)} + \dots)$$

$$= (\mathbf{P}^{(0)} \mathbf{P}^{(0)} + \lambda \mathbf{P}^{(0)} \mathbf{P}^{(1)} + \lambda \mathbf{P}^{(1)} \mathbf{P}^{(0)} + \dots) \quad (18)$$

Equating like powers of λ yields the expression 17, as well as our original expression 5. Using 17 allows us to restrict the elements of d_{pq}, utilizing the nature of the zeroth order density matrix given in 8. As an example, consider the element d_{ii}:

$$d_{ii} \propto P_{ii}^{(1)} = \sum_q \{ P_{iq}^{(0)} P_{qi}^{(1)} + P_{iq}^{(1)} P_{qi}^{(0)} \}$$

$$= P_{ii}^{(0)} P_{ii}^{(1)} + P_{ii}^{(1)} P_{ii}^{(0)}$$

$$= P_{ii}^{(1)} + P_{ii}^{(1)}$$

$$(19)$$

which is only true if $P_{ii}^{(1)} = 0$. Similar arguments show that the only contributing blocks of d_{pq} are d_{ia} and d_{ai}. In other words, the only contributions to the TDHF equations are the occupied-virtual and virtual-occupied blocks. All virtual-virtual and occupied-occupied blocks are necessarily zero. With this in mind, along with the diagonal nature of the unperturbed Fock matrix, yields

$$F_{aa}^{(0)} x_{ai} - x_{ai} F_{ii}^{(0)} + \left(f_{ai} + \sum_{bj} \left[\frac{\partial F_{ai}^{(0)}}{\partial P_{bj}} x_{bj} + \frac{\partial F_{ai}^{(0)}}{\partial P_{jb}} y_{bj} \right] \right) P_{ii}^{(0)} = \omega x_{ai} \quad (20)$$

and

$$F_{ii}^{(0)} y_{ai} - y_{ai} F_{aa}^{(0)} - P_{ii}^{(0)} \left(f_{ia} + \sum_{bj} \left[\frac{\partial F_{ia}^{(0)}}{\partial P_{bj}} x_{bj} + \frac{\partial F_{ia}^{(0)}}{\partial P_{jb}} y_{bj} \right] \right) = \omega y_{ai} \quad (21)$$

with $x_{ai} = d_{ai}$ and $y_{ai} = d_{ia}$, as is convention. The derivatives inside the expression evaluate as follows:

$$\sum_{rs} \frac{\partial F_{pq}}{\partial P_{rs}} = \sum_{rs} \frac{\partial}{\partial P_{rs}} \left(H_{pq}^{core} + P_{rs}[(pq|sr) - (pr|sq)] \right)$$

$$= (pq|sr) - (pr|sq) = (pq||sr) \tag{22}$$

Finally, we make the assumption that the perturbation is infinitely small, which sends $f_{ai} = f_{ia} \to 0$, and we recover (recognizing that $F_{pp}^{(0)} = \epsilon_p$ and $P_{ii}^{(0)} = 1$):

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & -\mathbf{A} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & \mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \tag{23}$$

Which is the non-Hermitian eigenvalue TDHF equation. The elements of $\mathbf{A}$ and $\mathbf{B}$ are

$$A_{ia,jb} = \delta_{ij}\delta_{ab}(\epsilon_a - \epsilon_i) + (ai||jb) \tag{24}$$

and

$$B_{ia,jb} = (ai||bj) \tag{25}$$