Polarization Propagator and Equation of Motion Methods

Joshua Goings
Department of Chemistry, University of Washington

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1 Equation of Motion (EOM) derivation of RPA

Given an *exact* ground state, we can say that

$$H|n\rangle = E_n|n\rangle \tag{1}$$

Define operator $Q_n^\dagger$ and Q_n:

$$|n\rangle = Q_n^\dagger|0\rangle, \qquad Q_n|0\rangle = 0 \implies Q_n^\dagger = |n\rangle\langle 0| \tag{2}$$

These operators generate excited states from the ground state (*not* excited determinants, as in the case of post-HF correlation methods). So it is clear that, when acting on an exact ground state:

$$[H, Q_n^\dagger]|0\rangle = (E_n - E_0)Q_n^\dagger|0\rangle = \hbar\omega_{0n}Q_n^\dagger|0\rangle \tag{3}$$

Multiply on left by arbitrary state of form $\langle 0|\delta Q$, giving

$$\langle 0|[\delta Q, [H, Q_n^\dagger]]|0\rangle = \hbar\omega_{0n}\langle 0|[\delta Q, Q_n^\dagger]|0\rangle \tag{4}$$

Where we have made use of the fact that $\langle 0|Q_n^\dagger = \langle 0|HQ_n^\dagger = 0$. Note that is we express Q by particle-hole operators $a_p^\dagger a_q$, $a_p^\dagger a_q^\dagger a_r a_s$ with coefficients C_{pq} and C_{pqrs}, then δQ is given by $\frac{\partial Q}{\partial C}\delta C$ for arbitrary variations δC. These are in principle exact, since $\delta Q|0\rangle$ exhausts the whole Hilbert space, such that the above equation corresponds to the full Schrödinger equation. Tamm-Dancoff (or Configuration Interaction Singles) can be obtained by approximating $|0\rangle \to |\mathrm{HF}\rangle$ and the operator $Q_n^\dagger = \sum\limits_{ia} C_{ia}a_a^\dagger a_i$, restricting ourselves to 1p-1h excitations. Thus $\delta Q|0\rangle = \sum_{ia} a_a^\dagger a_i|\mathrm{HF}\rangle\delta C_{ai}$, ($\delta C_{ai}$ cancels), and

$$\sum_{bj}\langle \mathrm{HF}|[a_i^\dagger a_a, [H, a_b^\dagger a_j]]|\mathrm{HF}\rangle C_{jb} = \hbar\omega\langle \mathrm{HF}|[a_i^\dagger a_a, a_a^\dagger a_i]|\mathrm{HF}\rangle C_{ia} \tag{5}$$

These are the CIS equations. Put another way:

$$\sum_{bj}\left\{(\epsilon_a - \epsilon_i)\delta_{ab}\delta_{ij} + \langle aj||ib\rangle\right\}C_{bj} = E^{CIS}C_{ai} \tag{6}$$

Similarly, for RPA/TDHF, if we consider a ground state containing 2p-2h correlations, we can not only create a p-h pair, but also destroy one. Thus (choosing the minus sign for convenience):

$$Q_n^\dagger = \sum_{ia} X_{ia}a_a^\dagger a_i - \sum_{ia} Y_{ia}a_i^\dagger a_a, \qquad \mathrm{and} Q_n|RPA\rangle = 0 \tag{7}$$

So instead of the basis of only single excitations, and therefore one matrix C_{ia}, we work in a basis of single excitations and single de-excitations, and have two matrices X_{ia} and Y_{ia}. We also have two kinds of variations $\delta Q|0\rangle$, namely $a_a^\dagger a_i|0\rangle$ and $a_i^\dagger a_a|0\rangle$. This gives us two sets of equations:

$$\langle \mathrm{RPA}|[a_i^\dagger a_a, [H, Q_n^\dagger]]|\mathrm{RPA}\rangle = \hbar\omega\langle \mathrm{RPA}|[a_i^\dagger a_a, Q_n^\dagger]|\mathrm{RPA}\rangle$$

$$\langle \text{RPA}|[a_a^\dagger a_i,[H,Q_n^\dagger]]|\text{RPA}\rangle = \hbar\omega\langle \text{RPA}|[a_a^\dagger a_i, Q_n^\dagger]|\text{RPA}\rangle \tag{8}$$

These contain only expectation values of our four Fermion operators, which cannot be calculated since we still do not know $|\text{RPA}\rangle$. Thus we assume $|\text{RPA}\rangle \to |\text{HF}\rangle$. This gives

$$\langle \text{RPA}|[a_i^\dagger a_a, a_b^\dagger a_j]|\text{RPA}\rangle = \langle \text{HF}|[a_i^\dagger a_a, a_b^\dagger a_j]|\text{HF}\rangle = \delta_{ij}\delta_{ab} \tag{9}$$

The probability of finding states $a_a^\dagger a_i|0\rangle$ and $a_i^\dagger a_a|0\rangle$ in excited state $|n\rangle$, that is, the p-h and h-p matrix elements of transition density matrix $\rho^{(1)}$ are:

$$\rho_{ai}^{(1)} = \langle 0|a_i^\dagger a_a|n\rangle \simeq \langle \text{HF}|[a_i^\dagger a_a, Q_n^\dagger]|\text{HF}\rangle = X_{ia} \tag{10}$$

$$\rho_{ia}^{(1)} = \langle 0|a_a^\dagger a_i|n\rangle \simeq \langle \text{HF}|[a_a^\dagger a_i, Q_n^\dagger]|\text{HF}\rangle = Y_{ia} \tag{11}$$

Thus altogether

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} = \hbar\omega \begin{bmatrix} \mathbf{1} & \mathbf{0} \\ \mathbf{0} & -\mathbf{1} \end{bmatrix} \begin{bmatrix} \mathbf{X} \\ \mathbf{Y} \end{bmatrix} \tag{12}$$

with

$$A_{ia,jb} = \langle \text{HF}|[a_i^\dagger a_a, [H, a_b^\dagger a_j]]|\text{HF}\rangle \tag{13}$$

and

$$B_{ia,jb} = -\langle \text{HF}|[a_i^\dagger a_a, [H, a_j^\dagger a_b]]|\text{HF}\rangle \tag{14}$$

which are the TDHF/RPA equations.