TDDFT Routines

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1 RPA matrix equations

We have $\mathbf{A}_{ia,jb}$ and $\mathbf{B}_{ia,jb}$ defined as:

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (\underline{ia}||\underline{jb}) \tag{1}$$

$$\mathbf{B}_{ia,jb} = (\underline{ia}||\underline{bj}) \tag{2}$$

1.1 Direct approximation

In the divert approximation, which we are working with because it is simpler to start with, this becomes:

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + (\underline{ia}|\underline{jb}) \tag{3}$$

$$\mathbf{B}_{ia,jb} = (\underline{ia}|\underline{bj}) \tag{4}$$

After the spin integration, we get:

$$\mathbf{A}_{ia,jb} = \delta_{ij}\delta_{ab}(\varepsilon_a - \varepsilon_i) + 2(ia|jb) \tag{5}$$

$$\mathbf{B}_{ia,jb} = 2(ia|bj) \tag{6}$$

We build the eigenvalue equation:

$$\begin{bmatrix} A & B \\ -B & -A \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} = \omega \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} \begin{bmatrix} X \\ Y \end{bmatrix} \tag{7}$$

1.2 Tamm-Dancoff approximation

In the Tamm-Dancoff approximation, we neglect $\mathbf{B}$, which means that we have:

$$\mathbf{AX} = \omega\mathbf{X} \tag{8}$$

The eigenvalues ω are the excitation energies, but we need to do some work to find the excitation vectors V^{μ}_{pq}. However, we will use the eigenvectors from this matrix equation to build the excitation vectors.

1.3 Building the excitation doctors

First, we consider within the direct approximation:

$$\mathbf{W}_{p,q,ia} = \sum_{\underline{p,q,i,a}} (\underline{pq}|\underline{ia}) \tag{9}$$

1.3.1 Spin integration

$|\Phi^a_i\rangle$ has the CSF

$$|\Phi_{singlet}\rangle = \frac{1}{\sqrt{2}}(|\Phi^{a\alpha}_{i\alpha}\rangle + \left|\Phi^{a\beta}_{i\beta}\right\rangle) \tag{10}$$

We want to consider something like:

$$\langle\Phi_0| \frac{1}{4}\sum_{pqrs} V_{pq\underline{rs}} a^\dagger_p a^\dagger_q a_s a_r \frac{1}{\sqrt{2}}(a^{\dagger\alpha}_a a^\alpha_i + a^{\dagger\beta}_a a^\beta_i) |\Phi_0\rangle \tag{11}$$

Consolidating constants out front and distributing the CSF terms:

$$\frac{1}{4\sqrt{2}} V_{pq\underline{rs}} \langle\Phi_0| a^\dagger_p a^\dagger_q a_s a_r a^{\dagger\alpha}_a a^\alpha_i |\Phi_0\rangle + \frac{1}{4\sqrt{2}} V_{pq\underline{rs}} \langle\Phi_0| a^\dagger_p a^\dagger_q a_s a_r a^{\dagger\beta}_a a^\beta_i |\Phi_0\rangle \tag{12}$$

Let's consider the first term:

$$\frac{1}{4\sqrt{2}}\sum_{pqrs} V_{pq\underline{rs}} \langle\Phi_0| a^\dagger_p a^\dagger_q a_s a_r a^{\dagger\alpha}_a a^\alpha_i |\Phi_0\rangle \tag{13}$$