Dynamic Correlations in Interacting Electrons

5/19/20

Recap of "dynamic correlations in electron liquids" in 1988, which forms the basis of divide-conquer-recombine (DCR) nonadiabatic quantum molecular dynamics (NAQMD).

— System Hamiltonian

$$\hat{H} = \sum_{\sigma} \int d\mathbf{r}\, \hat{\psi}_{\sigma}^{+}(\mathbf{r}) \left(-\frac{\hbar^2}{2m}\nabla^2 + v_{nuc}(\mathbf{r}) \right) \hat{\psi}_{\sigma}(\mathbf{r})$$

$$+ \frac{1}{2} \sum_{\sigma\sigma'} \int d\mathbf{r} \int d\mathbf{r}'\, \hat{\psi}_{\sigma}^{+}(\mathbf{r})\, \hat{\psi}_{\sigma'}^{+}(\mathbf{r}')\, v(|\mathbf{r}-\mathbf{r}'|)\, \hat{\psi}_{\sigma'}(\mathbf{r}')\, \hat{\psi}_{\sigma}(\mathbf{r}) \qquad (1)$$

where $\hat{\psi}_{\sigma}^{+}(\mathbf{r})$ and $\hat{\psi}_{\sigma}(\mathbf{r})$ are creation and annihilation operators for an electron with spin σ at position $\mathbf{r}$, $v_{nuc}(\mathbf{r})$ is the potential exerted by nuclei, and

$$v(r) = \frac{e^2}{r} \qquad (2)$$

is the Coulombic interaction.

— Generating functional

To formulate many-body correlations using functional derivatives, we define an expectation value of an arbitrary operator $\hat{O}$ in the presence of an external potential $\phi(1,1')$ in the ground state $|0\rangle$ as

$$\langle \hat{O}(t) \rangle = \frac{\langle 0 | T[\hat{O}_H(t) \hat{S}] | 0 \rangle}{\langle 0 | \hat{S} | 0 \rangle} \tag{3}$$

where T is the time-ordering operator,

$$\hat{O}_H(t) = e^{i\hat{H}t/\hbar} \hat{O} e^{-i\hat{H}t/\hbar}, \tag{4}$$

and the scattering operator $\hat{S}$ is

$$\hat{S} = T \exp\left[-\frac{i}{\hbar} \sum_{\sigma} \int d1 \int d1' \, \hat{\psi}^{+}_{H\sigma}(1) \, \phi(1,1') \, \hat{\psi}_{H\sigma}(1') \right] \tag{5}$$

Here, we have introduce a short hand notation, $1 \equiv (\mathbf{r}_1, t_1)$, for spatial position $\mathbf{r}_1$ and time t_1.

— Response functions

We define ν-body response functions ($\nu = 2, 3, \ldots$) as

$$\chi^{(\nu)}(1,1';\cdots;\nu,\nu') = \frac{\delta^{\nu-1}}{\delta\phi(\nu,\nu')\cdots\delta\phi(2,2')} \sum_\sigma \langle T[\hat{\psi}_\sigma^\dagger(1)\hat{\psi}_\sigma(1')]\rangle\Big|_{\phi\to 0} \quad (6)$$

In particular

$$\chi(1,2) = \chi^{(2)}(1^+,1;2^+,2) \quad (7)$$

is the density response function, where $1^+ = (\mathbf{r}_1, t_1+0)$ with 0 being positive infinitesimal.

— Equation-of-motion (EOM) for single-particle Green's function (SPGF)

Single-particle Green's function is defined as

$$\mathcal{G}(1,1') = -\frac{i}{2}\sum_\sigma \langle T[\hat{\psi}_\sigma(1)\hat{\psi}_\sigma^\dagger(1')]\rangle \quad (8)$$

Equation of motion for $\mathcal{G}$, along with the definition of response function, yields [5/2/88, cf., Martin & Schwinger Phys. Rev. 115, 1342 ('59); Baym & Kadanoff Phys. Rev. 124, 287 ('61); Nakano & Ichimaru, Phys. Rev. B 39, 4930 ('89); Martin et al., "Interacting Electrons" (Cambridge Univ. Press, '16)] the so-called Dyson equation

(Dyson equation)

$$\mathcal{G}^{-1}(1,1') = \mathcal{G}_0^{-1}(1,1') - \frac{1}{\hbar}\Phi(1,1') - \frac{1}{\hbar}v(1,\bar{2})\langle\rho(\bar{2})\rangle\delta(1,1') - \Sigma(1,1') \tag{9}$$

where

$$\mathcal{G}_0^{-1}(1,1') = \left[i\frac{\partial}{\partial t_1} + \frac{\hbar}{2m}\nabla_1^2\right]\delta(1,1') \tag{10}$$

and the self-energy is

$$\Sigma(1,1') = -\frac{1}{2}v(1^+,\bar{2})\chi^{(2)}(\bar{3},1;\bar{2}^+,\bar{2})\mathcal{G}^{-1}(\bar{3},1') \tag{11}$$

Here, integration with respect to the barred indices are implied, and

$$v(1,2) = v(|\mathbf{r}_1 - \mathbf{r}_2|)\,\delta(t_1 - t_2) \tag{12}$$

– Correlation potentials

We define ν-body correlation potentials ($\nu=2,3,\dots$) as

$$\Xi^{(\nu)}(1,1';\dots;\nu,\nu') = \frac{\delta^{\nu-1}}{\delta\mathcal{G}(\nu,\nu')\cdots\delta\mathcal{G}(2,2')}\Sigma(1,1') \tag{13}$$

※ Note that $\Xi^{(\nu)}$ represents the intrinsically ν-body and higher-order correlations. In particular, $\Xi^{(2)}$ is the exchange-correlation (xc) part of the "effective two-body interaction", with the latter also containing the long-range Coulomb interaction [Martin'16, Sec. 10.3].

- EOM for two-body response function

EOM for $\chi^{(2)}$, along with the defintion of correlation potentials, yields the so-called Bethe-Salpeter equation.

(Bethe-Salpeter equation)

$$
\begin{aligned}
\chi^{(2)}(1,1';2,2') = & -\frac{2i}{\hbar}\mathcal{G}(1,2)\mathcal{G}(2',1') \\
& -\frac{2i}{\hbar}\mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3},1')v(\bar{3},\bar{4})\chi^{(2)}(\bar{4}^{+},\bar{4};2,2') \\
& +\mathcal{G}(1,\bar{3})\mathcal{G}(\bar{3}',1')\Xi^{(2)}(\bar{3},\bar{3}';\bar{4}\bar{4}')\chi^{(2)}(\bar{4}',\bar{4},2,2') \qquad (14)
\end{aligned}
$$

- Local approximation

In Eq. (14), the two-body correlation potential $\Xi^{(2)}$ is short-ranged compared with the direct Coulomb interaction v [Kohn & Sham, Phys. Rev. 140, A1133 ('65); Hedin, Phys. Rev. 139, A796 ('65)], which is a consequence of the quantum near-sightedness [Kohn, Phys. Rev. Lett. 76, 3168 ('96); Prodan & Kohn, PNAS 102, 11635 ('05)].

This leads to a local approximation,

$$\Xi^{(2)}(1,1';2,2') \simeq \tilde{\Xi}^{(2)}(1,2)\,\delta(1,1')\,\delta(2,2') \qquad (15)$$

[Nakano '89]. The local approximation, Eq. (15), provides a systematic, conserving approximation over the random phase approximation (RPA), in which $\Xi^{(2)}=0$. This is achieved the next level of hierarchical EOM beyond the one-body Dyson equation (9) and two-body Bethe-Salpeter equation (14); i.e., EOM for three-body response function:

$$\begin{aligned}\chi^{(3)}(1',1;2,2';3,3') = &-\frac{\hbar}{4}\left[\mathcal{G}^{-1}(\bar{4},\bar{6})\,\mathcal{G}^{-1}(\bar{6}',\bar{5})\,\mathcal{G}^{-1}(\bar{5}',\bar{4}') + \mathcal{G}^{-1}(\bar{4},\bar{5})\,\mathcal{G}^{-1}(\bar{5}',\bar{6})\,\mathcal{G}^{-1}(\bar{6}',\bar{4}')\right] \\ &\times \chi^{(2)}(1',1;\bar{4}\bar{4}')\,\chi^{(2)}(\bar{5}',\bar{5},2,2')\,\chi^{(2)}(\bar{6}',\bar{6},3,3') \\ &-\frac{\hbar}{4}\,\Xi^{(3)}(\bar{4},\bar{4}';\bar{5},\bar{5}';\bar{6},\bar{6}') \\ &\times \chi^{(2)}(1',1;\bar{4},\bar{4}')\,\chi^{(2)}(\bar{5}',\bar{5},2,2')\,\chi^{(2)}(\bar{6}',\bar{6},3,3')\end{aligned} \qquad (16)$$

With the lowest-order approximation, $\Xi^{(3)} = 0$, for $\chi^{(3)}$, the local approximation to $\Xi^{(2)}$, Eq. (15), provides a closed form approximations for $\mathcal{G}$ and $\chi^{(2)}$ beyond RPA, which is named dynamic hypernetted-chain (DHNC) approximation [Nakano'89].