Non-self-consistent Exact Exchange Correction

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– Kohn-Sham basis

We start with a self-consistent (SC) solution of the Kohn-Sham (KS) equation using the generalized gradient approximation (GGA) as the exchange-correlation (xc) functional.

$$h_{KS}(\mathbf{r})\phi_{s\sigma}(\mathbf{r}) = \epsilon_{s\sigma}\phi_{s\sigma}(\mathbf{r}) \tag{1}$$

$$h_{KS}(\mathbf{r}) = -\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + \underbrace{\int d\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}}_{v_H(\mathbf{r})} + \underbrace{\frac{\delta E_{xc}^{GGA}}{\delta\rho(\mathbf{r})}}_{v_{xc}^{GGA}(\mathbf{r})} \tag{2}$$

$$\rho(\mathbf{r}) = \sum_{s\sigma} f_{s\sigma}|\phi_{s\sigma}(\mathbf{r})|^2 \tag{3}$$

– Non-self-consistent long-range exact exchange Hamiltonian

We now use the SC KS solution to obtain a non-self-consistent (NSC) solution to a generalized Kohn-Sham (GKS) equation using a range-separated hybrid exact exchange functional.

$$h_{GKS}(\mathbf{r})\phi'_{s\sigma}(\mathbf{r}) = \epsilon'_{s\sigma}\phi'_{s\sigma}(\mathbf{r}) \tag{4}$$

$$\hat{h}_{GKS}(\mathbf{r})\,\phi(\mathbf{r}) = \left[-\frac{\nabla^2}{2} + v_{ion}(\mathbf{r}) + v_H(\mathbf{r})\right]\phi(\mathbf{r})$$

$$- \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma}(\mathbf{r}')\phi(\mathbf{r}')\phi_{i\sigma}(\mathbf{r})$$

$$+ \underbrace{\frac{\delta(E_{xc}^{GGA} - E_x^{GGA,lr})}{\delta\rho(\mathbf{r})}}_{(v_{xc}^{GGA} - v_x^{GGA,lr})[\rho](\mathbf{r})} \phi(\mathbf{r}) \qquad (5)$$

$$= \left[\hat{h}_{KS}(\mathbf{r}) - v_x^{GGA,lr}[\rho](\mathbf{r})\right]\phi(\mathbf{r})$$

$$- \sum_{i\sigma}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma}(\mathbf{r}')\phi(\mathbf{r}')\phi_{i\sigma}(\mathbf{r}) \qquad (6)$$

Note the NSC-GKS Hamiltonian contains the SC-KS orbitals, $\{\phi_{s\sigma}(\mathbf{r})\}$.

– NSC-GKS orbitals

We expand the eigenstates of the NSC-GKS Hamiltonian, Eq.(4), in terms of the SC-KS orbitals $\{\phi_{s\sigma}(\mathbf{r})\}$:

$$\phi'_{s\sigma}(\mathbf{r}) = \sum_{t\tau} C_{t\tau}^{(s\sigma)} \phi_{t\tau}(\mathbf{r}) \qquad (7)$$

Substituting Eq.(7) in (4),

$$\sum_{t\tau} C_{t\tau}^{(s\sigma)} [\underbrace{\hat{h}_{KS}(\mathbf{r})}_{\epsilon_{t\tau}} - v_x^{GGA,lr}[\rho](\mathbf{r})]\,\phi_{t\tau}(\mathbf{r})$$

$$- \sum_{t\tau} C_{t\tau}^{(s\sigma)} \sum_{i\sigma'}^{occ} \int d\mathbf{r}' \frac{\mathrm{erf}(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|} \phi^*_{i\sigma'}(\mathbf{r}')\phi_{t\tau}(\mathbf{r}')\phi_{i\sigma'}(\mathbf{r}) = \epsilon'_{s\sigma} \sum_{t\tau} C_{t\tau}^{(s\sigma)} \phi_{t\tau}(\mathbf{r})$$

(8)

$\int d\mathbf{r}\,\phi^*_{u\lambda}(\mathbf{r}) \times$ Eq. (8)

(∵ spin integration)

$$\sum_{t\tau} C^{(s\sigma)}_{t\tau}\left[\epsilon_{t\tau}\delta_{ut}\delta_{\lambda\tau} - \delta_{\lambda\tau}\langle u\lambda|v_x^{GGA,lr}[\rho]|t\tau\rangle\right]$$

$$-\sum_{t\tau} C^{(s\sigma)}_{t\tau}\sum_{i\sigma'}^{occ}\underbrace{\iint d\mathbf{r}\,d\mathbf{r}'\,\phi^*_{u\lambda}(\mathbf{r})\phi_{i\sigma'}(\mathbf{r})\frac{erfc(\mu|\mathbf{r}-\mathbf{r}'|)}{|\mathbf{r}-\mathbf{r}'|}\phi^*_{i\sigma'}(\mathbf{r}')\phi_{t\tau}(\mathbf{r}')}_{\underbrace{\delta_{\lambda\sigma'}\delta_{\sigma'\tau}}_{\delta_{\lambda\tau}\delta_{\tau\sigma'}}[\phi^*_{u\lambda}\phi_{i\sigma'}|\frac{erf(\mu r)}{r}|\phi^*_{i\sigma'}\phi_{t\tau}]}$$

(∵ spin integration)

$$= \epsilon'_{s\sigma}\underbrace{\sum_{t\tau} C^{(s\sigma)}_{t\tau}\,\delta_{ut}\,\delta_{\lambda\tau}}_{C_{s\sigma,u\lambda}} \qquad (9)$$

$$\sum_{t\tau} C^{(s\sigma)}_{t\tau}\Big\{\underbrace{\epsilon_{t\tau}\delta_{ut}\delta_{\lambda\tau} - \delta_{\lambda\tau}\langle u\lambda|v_x^{GGA,lr}[\rho]|t\tau\rangle - \delta_{\lambda\tau}\sum_{i}^{occ}[\phi^*_{u\lambda}\phi_{i\tau}|\frac{erf(\mu r)}{r}|\phi^*_{i\tau}\phi_{t\lambda}]}_{H'_{u\lambda,t\tau}}\Big\} = \epsilon'_{s\sigma}C^{(s\sigma)}_{u\lambda}$$

$$\therefore \quad \sum_{t} H'_{u,t}\, C^{(s\lambda)}_{t\lambda} = \epsilon'_{s\lambda}C^{(s\lambda)}_{u\lambda} \qquad (10)$$

$$H'_{u,t} = \epsilon_{t\tau}\delta_{ut} - \langle u\lambda|v_x^{GGA,lr}[\rho]|t\lambda\rangle - \sum_{i}^{occ}[\phi^*_{u\lambda}\phi_{i\lambda}|\frac{erf(\mu r)}{r}|\phi^*_{i\lambda}\phi_{t\lambda}] \qquad (11)$$

In summary,

$$\phi'_{s\sigma}(\mathbf{r}) = \sum_t C_t^{(s)} \phi_{t\sigma}(\mathbf{r}) \tag{12}$$

$$\sum_u H'_{t,u} C_u^{(s)} = \epsilon'_{s\sigma} C_t^{(s)} \tag{13}$$

$$H'_{t,u} = \delta_{t,u}\epsilon_{u\sigma} - \int d\mathbf{r}\, \phi^*_{t\sigma}(\mathbf{r})\, v_x^{GGA,lr}[\rho](\mathbf{r})\, \phi_{u\sigma}(\mathbf{r}) - \sum_i^{occ} \left[\phi^*_{t\sigma}\phi_{i\sigma} \middle| \frac{erf(\mu r)}{r} \middle| \phi^*_{i\sigma}\phi_{u\sigma}\right] \tag{14}$$

where the Coulomb-like integral is defined as

$$[f|h(\mathbf{r})|g] = \iint d\mathbf{r}\, d\mathbf{r}'\, f(\mathbf{r})\, h(|\mathbf{r}-\mathbf{r}'|)\, g(\mathbf{r}') \tag{15}$$

$$\phi'_{s\sigma}(\mathbf{r}) = \sum_t \phi_{t\sigma}(\mathbf{r}) \underbrace{U_{ts}}_{= C_t^{(s)}}$$

$$\int d\mathbf{r}\, \phi'^*_{s\sigma}(\mathbf{r})\, \phi'_{s'\sigma}(\mathbf{r}) = \sum_{tt'} \int d\mathbf{r}\, \phi^*_{t\sigma}(\mathbf{r})\, U^*_{ts}\, \phi_{t'\sigma}(\mathbf{r})\, U_{t's'}$$

$$= \sum_{tt'} U^*_{ts} U_{t's'} \underbrace{\int d\mathbf{r}\, \phi^*_{t\sigma}(\mathbf{r})\, \phi_{t'\sigma}(\mathbf{r})}_{\delta_{tt'}}$$

$$= \sum_t U^*_{ts} U_{ts'} = \sum_t (U^\dagger)_{st} U_{ts'} = \delta_{ss'}$$

$\therefore \mathbb{U}^\dagger \mathbb{U} = \mathbb{I}$, *unitary*

$$\sum_u H'_{tu} U_{us} = U_{ts}\, \epsilon'_{s\sigma}$$