Time Dependent Density Functional Pertubation Theory for Magnetic excitations

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A. Noncollinear generalization of DFT

The noncollinear spin version of the Kohn-Sham equation can be written as

$$\left[(-\frac{\nabla^2}{2}+2\sum_\alpha\int\frac{\rho_{\alpha\alpha}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}')I+\tilde{v}(\mathbf{r})+\frac{\delta E_{xc}}{\delta\rho(\mathbf{r})}\right]\begin{pmatrix}\psi^1\\ \psi^2\end{pmatrix}=\epsilon_i\begin{pmatrix}\psi^1\\ \psi^2\end{pmatrix} \tag{1}$$

where I is 2×2 unit matrix. $\tilde{v}(\mathbf{r})$ and exchange-correlation potential become 2×2 matrix. The density matrix $\rho(\mathbf{r})$ can be written as

$$\rho_{\alpha\beta}(\mathbf{r})=\sum_i\psi_i^{\alpha*}(\mathbf{r})\psi_i^{\beta}(\mathbf{r}),\ \text{where } \alpha,\beta=1,2 \tag{2}$$

which using Pauli matrix σ, can be decomposed into a scalar and a vectorial part corresponding to the charge and magnetization density:

$$\rho(\mathbf{r})=\frac{1}{2}(n(\mathbf{r})I+\boldsymbol{\sigma}\cdot\mathbf{m}(\mathbf{r}))=\frac{1}{2}\begin{pmatrix}n(\mathbf{r})+m_z(\mathbf{r}) & m_x(\mathbf{r})-im_y(\mathbf{r})\\ m_x(\mathbf{r})+im_y(\mathbf{r}) & n(\mathbf{r})-m_z(\mathbf{r})\end{pmatrix}$$

Likewise, the potential matrix can then be written in the form of a scalar potential and a magnetic field $\mathbf{B}(\mathbf{r})$

$$\tilde{v(\mathbf{r})}=v(\mathbf{r})I+\mu_B\boldsymbol{\sigma}\cdot\mathbf{B}(\mathbf{r}) \tag{3}$$

$$\tilde{v_{xc}(\mathbf{r})}=v_{xc}(\mathbf{r})I+\mu_B\boldsymbol{\sigma}\cdot\mathbf{B_{xc}}(\mathbf{r}) \tag{4}$$

where μ_B is the Bohr magneton. Finally, to simplify the notation, the noncollinear spin Kohn-Sham equation can be recast as,

$$\left[\left(-\frac{\nabla^2}{2}+V_{eff}(\mathbf{r})\right)I+\mu_B\boldsymbol{\sigma}\cdot\mathbf{B}_{eff}(\mathbf{r})\right]\overrightarrow{\psi}_i(\mathbf{r})=\epsilon_i\overrightarrow{\psi}_i(\mathbf{r}) \tag{5}$$

Where V_{eff} is the total scalar potential and $\mathbf{B}_{eff}$ is the total effective magnetic field.

B. Local approximation to exchange-correlation functional with noncollinear spin density

The collinear exchange-correlation functional is in the form of

$$E_{xc}=E_{xc}\{\rho_1,\rho_2\}=\int n(\mathbf{r})\epsilon_{xc}[\rho_1(\mathbf{r}),\rho_2(\mathbf{r})]d\mathbf{r} \tag{6}$$

where $n(\mathbf{r})=\rho_1(\mathbf{r})+\rho_2(\mathbf{r})$. ρ_1, ρ_2 is the up and down spin density respectively. In the noncollinear spin case, $\rho_{\alpha\beta}$ is not necessarily diagonal. However, assume there is a unitary transformation, U, which can diagonalize it locally, i.e. for i=1, 2,

$$\sum_{\alpha\beta}U_{i,\alpha}\rho_{\alpha\beta}U^\dagger_{\beta,i}=\rho_i \tag{7}$$

with all quantities dependent on $\mathbf{r}$. U can be expressed in spin-$\frac{1}{2}$ rotation matrix with rotation angle θ and ϕ. Then the effective single-particle potential matrix can be written as,

$$W_{eff}(\mathbf{r})=V_{eff}(\mathbf{r})I+\Delta V(\mathbf{r})\tilde{\sigma}_z \tag{8}$$

where $\tilde{\sigma}_z$ is the z component of the Pauli matrix in a coordinate system which is rotated by the polar angles θ and ϕ with respect to some global coordination system,

$$\tilde{\sigma}_z = \begin{bmatrix} \cos\theta & e^{-i\phi}\sin\theta \\ e^{i\phi}\sin\theta & -\cos\theta \end{bmatrix}$$

By mapping to Eq. 5, the local effective magnetic field is expressed as

$$B^z_{eff}(\mathbf{r})\mu_B = \Delta V(\mathbf{r})\cos\theta \tag{9}$$

$$B^x_{eff}(\mathbf{r})\mu_B = \Delta V(\mathbf{r})\cos\phi\sin\theta \tag{10}$$

$$B^y_{eff}(\mathbf{r})\mu_B = \Delta V(\mathbf{r})\sin\phi\sin\theta \tag{11}$$

$V_{eff}(\mathbf{r})$ is given by

$$V_{eff}(\mathbf{r}) = v(\mathbf{r}) + 2\int \frac{n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}' + \frac{1}{2}[v_{xc1}(\mathbf{r}) + v_{xc2}(\mathbf{r})] \tag{12}$$

furthermore,

$$v_{xci}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta\rho_i} = \epsilon_{xc}(\rho_1,\rho_2) + n\frac{\partial\epsilon_{xc}}{\partial\rho_i} \tag{13}$$

and

$$\Delta V(\mathbf{r}) = \frac{1}{2}[v_{xc1}(\mathbf{r}) - v_{xc2}(\mathbf{r})] \tag{14}$$

we can see that when $\theta = \phi = 0$ holds globally, W_{eff} goes back to the form of collinear spin case.

C. First-order time dependent perturbation theory

If the perturbed wave function is written as $[\overrightarrow{\psi}_i(\mathbf{r}) + \delta\overrightarrow{\psi}_i(\mathbf{r},t)]e^{-i\epsilon_i t}$, the equation for standard time dependent first-order perturbation theory is then

$$(H - i\partial_t I)\delta\overrightarrow{\psi}_i(\mathbf{r},t) + (\delta V_{eff}I + \mu_B\delta\mathbf{B}_{eff}\sigma)\overrightarrow{\psi}_i(\mathbf{r}) = 0 \tag{15}$$

where $\delta\overrightarrow{\psi}_i(\mathbf{r},t)$ is the first order change of the wave function, δV_{eff} and $\delta\mathbf{B}_{eff}$ are the first-order changes of effetive electric potential and magnetic field due to the external perturbation. In frequency space, Eq. 15 is

$$(H - \epsilon_i + \omega)\delta\overrightarrow{\psi}_i(\mathbf{r},\omega) + [\delta V_{eff}(\mathbf{r},\omega) + \mu_B\sigma\delta\mathbf{B}_{eff}(\mathbf{r},\omega)]\overrightarrow{\psi}_i(\mathbf{r}) = 0 \tag{16}$$

If we write the bloch wave function as $\overrightarrow{\psi}^{\mathbf{k}}_n(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}\overrightarrow{u}^{\mathbf{k}}_n(\mathbf{r})$, then in the case of monochromatic perturbations $\delta B_{ext}(\mathbf{r},t) = \delta\mathbf{b}e^{i\mathbf{q_0}\cdot\mathbf{r}}e^{i\omega_0 t}e^{-\eta t} + c.c.$, Eq. 16 can be written as

$$(H^{\mathbf{k+q}} - \epsilon^{\mathbf{k}}_i + \omega)\delta\overrightarrow{u}^{\mathbf{k+q}}_i(\mathbf{r},\omega) + [\delta V^{\mathbf{q}}_{eff}(\mathbf{r},\omega) + \mu_B\sigma\delta\mathbf{B}^{\mathbf{q}}_{eff}(\mathbf{r},\omega)]\overrightarrow{u}^{\mathbf{k}}_i(\mathbf{r}) = 0 \tag{17}$$

where $\delta\overrightarrow{u}^{\mathbf{k+q}}_i(\mathbf{r},\omega)$ is the periodic parts of $\mathbf{k}$+$\mathbf{q}$ Fourier component of the first order correction of the wave function, i.e. $\delta\overrightarrow{\psi}^{\mathbf{k+q}}_n(\mathbf{r}) = e^{i(\mathbf{k+q})\cdot\mathbf{r}}\delta\overrightarrow{u}^{\mathbf{k+q}}_n(\mathbf{r})$. The effective potential is written as $\delta V_{eff}(\mathbf{r},t) = \sum_{\mathbf{q},\omega}\delta V^{\mathbf{q}}_{eff}(\mathbf{r},\omega)e^{i(\mathbf{q}\cdot\mathbf{r}+\omega t)}$ with the effective magnetic field in the same form. The Fourier compoments of first-order change of charge density can be written as:

$$\delta n^{\mathbf{q}}(\mathbf{r},\omega) = \sum_{\mathbf{k}}[\overrightarrow{u}^{\mathbf{k}*}|I|\delta\overrightarrow{u}^{\mathbf{k+q}}(\mathbf{r},\omega) + \delta\overrightarrow{u}^{\mathbf{k-q}*}(\mathbf{r},-\omega)|I|\overrightarrow{u}^{\mathbf{k}}] \tag{18}$$

$$\delta n^{\mathbf{q}}(\mathbf{r},-\omega) = \sum_{\mathbf{k}}[\overrightarrow{u}^{\mathbf{k}*}|I|\delta\overrightarrow{u}^{\mathbf{k+q}}(\mathbf{r},-\omega) + \delta\overrightarrow{u}^{\mathbf{k-q}*}(\mathbf{r},\omega)|I|\overrightarrow{u}^{\mathbf{k}}] \tag{19}$$

$$\delta n^{-\mathbf{q}}(\mathbf{r},-\omega) = \sum_{\mathbf{k}}[\overrightarrow{u}^{\mathbf{k}*}|I|\delta\overrightarrow{u}^{\mathbf{k-q}}(\mathbf{r},-\omega) + \delta\overrightarrow{u}^{\mathbf{k+q}*}(\mathbf{r},\omega)|I|\overrightarrow{u}^{\mathbf{k}}] = \delta n^{\mathbf{q}*}(\mathbf{r},\omega) \tag{20}$$

$$\delta n^{-\mathbf{q}}(\mathbf{r},\omega) = \sum_{\mathbf{k}}[\overrightarrow{u}^{\mathbf{k}*}|I|\delta\overrightarrow{u}^{\mathbf{k-q}}(\mathbf{r},\omega) + \delta\overrightarrow{u}^{\mathbf{k+q}*}(\mathbf{r},-\omega)|I|\overrightarrow{u}^{\mathbf{k}}] = \delta n^{\mathbf{q}*}(\mathbf{r},-\omega) \tag{21}$$

where * means complex conjugate. The first order change of magnetization follows the same set of equations with unit matrix I substitued by Pauli matrix σ.

In the presence of time reversal symmetry, e.g. paramagnetic system without external magnetic field, $u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) = u^{-\mathbf{k}-\mathbf{q}*}(\mathbf{r},\omega)$. Eq. 18 can then be recasted as

$$\begin{aligned}
\delta n^{\mathbf{q}}(\mathbf{r},\omega) &= \sum_{\mathbf{k}}[u^{\mathbf{k}*}\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \delta u^{\mathbf{k}-\mathbf{q}*}(\mathbf{r},-\omega)u^{\mathbf{k}}] \quad (22)\\
&= \sum_{\mathbf{k}}[u^{\mathbf{k}*}\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \delta u^{-\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega)u^{-\mathbf{k}*}] \quad (23)\\
&= \sum_{\mathbf{k}}[u^{\mathbf{k}*}\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega)u^{\mathbf{k}*}] \quad (24)\\
&= \sum_{\mathbf{k}} u^{\mathbf{k}*}[\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega)] \quad (25)
\end{aligned}$$

Following the same logic, Eq. 19 can be recasted as

$$\begin{aligned}
\delta n^{\mathbf{q}}(\mathbf{r},-\omega) &= \sum_{\mathbf{k}}[u^{\mathbf{k}*}\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega) + \delta u^{\mathbf{k}-\mathbf{q}*}(\mathbf{r},\omega)u^{\mathbf{k}}] \quad (26)\\
&= \sum_{\mathbf{k}}[u^{\mathbf{k}*}\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega) + \delta u^{-\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega)u^{-\mathbf{k}*}] \quad (27)\\
&= \sum_{\mathbf{k}}[u^{\mathbf{k}*}\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega) + \delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega)u^{\mathbf{k}*}] \quad (28)\\
&= \sum_{\mathbf{k}} u^{\mathbf{k}*}[\delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) + \delta u^{\mathbf{k}+\mathbf{q}}(\mathbf{r},-\omega)] \quad (29)\\
&= \delta n^{\mathbf{q}}(\mathbf{r},\omega) \quad (30)
\end{aligned}$$

Now Eq. 17 can be solved in the **q** component of the effective potential with $\pm\omega$,

$$(H^{\mathbf{k}+\mathbf{q}} - \epsilon_i^{\mathbf{k}} \pm \omega)\overrightarrow{\delta u}_i^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\pm\omega) + [\delta V_{eff}^{\mathbf{q}}(\mathbf{r},\omega) + \mu_B\sigma\delta\mathbf{B}_{eff}^{\mathbf{q}}(\mathbf{r},\omega)]\overrightarrow{u}_i^{\mathbf{k}}(\mathbf{r}) = 0 \quad (31)$$

However, in a general system with noncollinear spin density or with the presence of an external magnetic field, time reversal is broken. In this case, Eq. 17 could be solved using a set of two equations,

$$\begin{aligned}
(H^{\mathbf{k}+\mathbf{q}} - \epsilon_i^{\mathbf{k}} + \omega)\overrightarrow{\delta u}_i^{\mathbf{k}+\mathbf{q}}(\mathbf{r},\omega) &+ [\delta V_{eff}^{\mathbf{q}}(\mathbf{r},\omega) + \mu_B\sigma\delta\mathbf{B}_{eff}^{\mathbf{q}}(\mathbf{r},\omega)]\overrightarrow{u}_i^{\mathbf{k}}(\mathbf{r}) = 0 \quad (32)\\
(H^{\mathbf{k}-\mathbf{q}} - \epsilon_i^{\mathbf{k}} - \omega)\overrightarrow{\delta u}_i^{\mathbf{k}-\mathbf{q}}(\mathbf{r},-\omega) &+ [\delta V_{eff}^{-\mathbf{q}}(\mathbf{r},-\omega) + \mu_B\sigma\delta\mathbf{B}_{eff}^{-\mathbf{q}}(\mathbf{r},-\omega)]\overrightarrow{u}_i^{\mathbf{k}}(\mathbf{r}) = 0 \quad (33)
\end{aligned}$$

with the charge density response $\delta n^{\mathbf{q}}(\mathbf{r},\omega)$ and $\delta n^{-\mathbf{q}}(\mathbf{r},-\omega)$ calculated using Eq. 18 and Eq. 20 respectively.

D. Plane wave basis