GW Theory

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I. LINEAR RESPONSE EXCITATIN THEORY: G_0W_0 THEORY

Within the linear response many body perturbation theory (MBPT), we first start with the electronic Hartree-Fock exchange static self-energy $\sum_{n\mathbf{k}}^{x}$. The matrix elements of this self-energy in the plane wave basis set are diagonal and can be expressed as [1, 2]

$$\sum\nolimits_{n\mathbf{k}}^{x} = \langle n\mathbf{k} \left| \sum\nolimits^{x} \right| n\mathbf{k} \rangle = -\sum_{m}^{occ} \int_{BZ} \frac{d\mathbf{q}}{(2\pi)^3} \sum_{\mathbf{G}} v\left(\mathbf{q}+\mathbf{G}\right) \times \left|\rho_{nm}\left(\mathbf{k},\mathbf{q},\mathbf{G}\right)\right|^2 f_{m(\mathbf{k}-\mathbf{q})} \tag{1}$$

in which $|n\mathbf{k}\rangle$ is the momentum state of n^{th} band, $\mathbf{q}$ are the transferred momenta, m are the number of occupied electronic bands, f is the Fermi function and ρ is the density matrix. $\mathbf{G}$ are the G-vectors with $v\left(\mathbf{q}+\mathbf{G}\right) = \frac{4\pi}{|\mathbf{q}+\mathbf{G}|^2}$ as the three-dimensional Coulomb potential in the Fourier transformed $\mathbf{q}$-plane.
At this level, the Hartree-Fock contribution to the ground state Kohn-Sham energy eigenvalues can be written as

$$E_{n\mathbf{k}}^{HF} = E_{n\mathbf{k}}^{DFT} + (\sum\nolimits_{n\mathbf{k}}^{x} - V_{n\mathbf{k}}^{xc}) \tag{2}$$

in which V_{nk}^{xc} is the exchange and correlation functional at the level of local density or generalized gradient approximation.
The GW approximation theory is the generalization of this Hartree-Fock theory achieved by replacing the bare static screening potential $v\left(\mathbf{r},\mathbf{r}'\right)$ by a dynamic screened interaction $\mathrm{W}\left(\mathbf{r},\mathbf{r}';\omega\right)$. We describe this scheme as follows: Using the time-ordered single-particle non-interacting Green's propagator G_0, the polarization within the random phase approximation (RPA, i.e., using Hartree-kernel) is first calculated

$$\mathcal{P}\left(\mathbf{r},\mathbf{r}'';\tau\right) = -i\mathrm{G}_0\left(\mathbf{r},\mathbf{r}';\tau\right)\mathrm{G}_0\left(\mathbf{r}',\mathbf{r};-\tau\right) \tag{3}$$

where $\tau = t - t'$, while t and t' are the time developments in the Green's propagator. Note that Eqn.(3) is summed over both the occupied and unoccupied states in the Fourier transformed ω-plane

$$\mathcal{P}\left(\mathbf{r},\mathbf{r}'';\omega\right) = \sum_{i}^{occ}\sum_{j}^{unocc} \psi_i^0\left(\mathbf{r}\right)\psi_j^{0*}\left(\mathbf{r}\right)\psi_i^{0*}\left(\mathbf{r}'\right)\psi_j^0\left(\mathbf{r}'\right) \times \left[\frac{1}{\omega + E_i^0 - E_j^0 + i\eta} - \frac{1}{\omega - E_i^0 + E_j^0 - i\eta}\right] \tag{4}$$

where the number η is infinitesimal real and positive number. The microscopic dielectric function is the convolution of $\mathcal{P}\left(\mathbf{r},\mathbf{r}'';\omega\right)$ with $v\left(\mathbf{r},\mathbf{r}'\right)$

$$\varepsilon\left(\mathbf{r},\mathbf{r}';\omega\right) = \delta\left(\mathbf{r}-\mathbf{r}'\right) - \int \mathcal{P}\left(\mathbf{r},\mathbf{r}'';\omega\right) v\left(\mathbf{r},\mathbf{r}''\right) d^3\mathbf{r}'' \tag{5}$$

From Eqn. (5), the inverse microscopic dielectric function $\varepsilon^{-1}\left(\mathbf{r},\mathbf{r}'';\omega\right)$ is obtained and is again convoluted with $v\left(\mathbf{r},\mathbf{r}'\right)$ to get

$$\mathrm{W}\left(\mathbf{r},\mathbf{r}';\omega\right) = \int \varepsilon^{-1}\left(\mathbf{r},\mathbf{r}'';\omega\right) v\left(\mathbf{r},\mathbf{r}''\right) d^3\mathbf{r}'' \tag{6}$$

Equation (6) signifies that a quasi-particle at $\mathbf{r}$ induces an effective screened interacting dynamic potential $\mathrm{W}\left(\mathbf{r},\mathbf{r}';\omega\right)$ at $\mathbf{r}'$. Once $\mathrm{W}\left(\mathbf{r},\mathbf{r}';\omega\right)$ is known, the GW self-energy is a final full frequency-axis convolution of non-interacting propagator G_0 with $\mathrm{W}\left(\mathbf{r},\mathbf{r}';\omega\right)$

$$\sum\nolimits^{\mathrm{GW}}\left(\mathbf{r},\mathbf{r}';\omega\right) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} \mathrm{G}_0\left(\mathbf{r},\mathbf{r}';\omega+\omega'\right)\mathrm{W}\left(\mathbf{r},\mathbf{r}';\omega'\right)e^{i\omega'\eta}d\omega' \tag{7}$$

Single shot GW or $\mathrm{G}_0\mathrm{W}_0$ is the condition when the non-interacting Green's function is used and the screened interaction W is only once iterated through RPA. Note that now, the screening W implicitly defines $\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}$ in Fourier transformed $\mathbf{q}$-plane. A pure correlational $\mathrm{G}_0\mathrm{W}$ self-energy can be extracted from Eqn. (7) as

$$\sum\nolimits^{c}\left(\mathbf{r},\mathbf{r}';\omega\right) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} \mathrm{G}_0\left(\mathbf{r},\mathbf{r}';\omega+\omega'\right)\mathrm{W}^{c}\left(\mathbf{r},\mathbf{r}';\omega\right)d\omega' \tag{8}$$

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leaving the pure exchange term as

$$\sum\nolimits^{x}(\mathbf{r},\mathbf{r}';\omega) = \frac{i}{2\pi}\int_{-\infty}^{+\infty} \mathrm{G}_0(\mathbf{r},\mathbf{r}';\omega+\omega')\, v(\mathbf{r},\mathbf{r}')\, e^{i\omega'\eta} d\omega' \tag{9}$$

in which $\mathrm{W}^{c}(\mathbf{r},\mathbf{r}';\omega) = \mathrm{W}(\mathbf{r},\mathbf{r}';\omega) - v(\mathbf{r},\mathbf{r}')$. Eqn. (9) can be computed analytically in both $\mathbf{q}$ and ω plane leading to Eqn. (1). Symbolically, the total GW self-energy is split into a respective exchange (Hartree-Fock) and correlational part as iGv+iG(W-v). Because of the presence of several poles of both G_0 and W, located infinitely close to the real-frequency axis, the above frequency integral Eqn. (7) becomes computationally expensive. What is then done is to replace $\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}$ with an effective inverse dielectric function model consisting of a single pole, essentially at the plasma frequency describing the collective charge-neutral excitation. This approximation is known as the "plasmon-pole model". There has been various such celebrated approximate models developed in the past like the Hybertsen-Louie (HL) [3], Godby-Needs (GN) [**?**], Linden-Horsch (LH) [4] and Engel-Farid (EF) [5], to name a few [6]. Out of these, the first two are the most common in practice. Here, we use the GN plasmon-pole model approximation since this is found to be most stable and fits the above inverse dynamic dielectric function and the corresponding QP energies very accurately when evaluated by the complete full-frequency integral [6].
The GN plasmon-pole model replace this $\varepsilon^{-1}_{\mathbf{G}\mathbf{G}'}$ with a single pole function of the form

$$\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega) \sim \delta_{\mathbf{G},\mathbf{G}'} + R_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) \left\{ \frac{1}{[\omega - \Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) + i0^{+}]} \; - \frac{1}{[\omega + \Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) + i0^{+}]} \right\} \tag{10}$$

The residuals $R_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ and the energy $\Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ parameters are generally obtained by fitting after calculating the RPA inverse dielectric matrix at two given frequencies ω=0 and at a user defined imaginary frequency ($i\omega'_p$), in which (ω'_p) is typically chosen such that it should be near to the plasmon frequency (ω_p). These two parameters are then evaluated as $R_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \frac{1}{2}\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=0)\,\Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q})$ and $\Omega_{\mathbf{G},\mathbf{G}'}(\mathbf{q}) = \omega'_p\sqrt{\frac{\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\omega'_p)}{\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=0)-\varepsilon^{-1}_{\mathbf{G},\mathbf{G}'}(\mathbf{q},\omega=\omega'_p)}}$. To account for the charge inhomogeneity, a local field effect was also employed along the in-plane periodic direction using a sufficient response block size cut-off.
Assuming that the difference between the QP and the mean-field energies are small, the nonlinear QP energy [1]

$$E^{QP}_{n\mathbf{k}} = E^{DFT}_{n\mathbf{k}} + \left\langle n\mathbf{k} \middle| \sum\nolimits^{\mathrm{GW}}\left(\mathbf{r},\mathbf{r}';\omega = E^{QP}_{n\mathbf{k}}\right) - V^{xc} \middle| n\mathbf{k} \right\rangle \tag{11}$$

can be linearized [1, 7] by taking the first-order Taylor's series expansion around the Kohn-Sham DFT eigen-energies in order to get

$$E^{QP}_{n\mathbf{k}} = E^{DFT}_{n\mathbf{k}} + Z_{nk}\left\langle n\mathbf{k} \middle| \sum\nolimits^{\mathrm{GW}}\left(\mathbf{r},\mathbf{r}';\omega = E^{DFT}_{n\mathbf{k}}\right) - V^{xc} \middle| n\mathbf{k} \right\rangle \tag{12}$$

The QP lifetimes are the reciprocal of the imaginary part of $\sum^{\mathrm{GW}}_{n\mathbf{k}} = \left\langle n\mathbf{k} \middle| \sum^{\mathrm{GW}}\left(\mathbf{r},\mathbf{r}';\omega = E^{DFT}_{n\mathbf{k}}\right) \middle| n\mathbf{k} \right\rangle$. This factor

$$Z = \left[1 - \frac{d\sum^{\mathrm{GW}}_{n\mathbf{k}}}{d\omega}\right]^{-1} \tag{13}$$

with $0 \leq Z_{n\mathbf{k}} \leq 1$ is then the QP renormalized weight factor. Values of Z very close to 1 signifies a pure QP state. The corresponding spectral function

$$A_{n,\mathbf{k}}(\omega) = \frac{1}{\pi} \times \left|\Im\sum\nolimits^{\mathrm{GW}}_{n\mathbf{k}}\right| \times \left[\left[\omega - E^{DFT}_{n\mathbf{k}} - \left(\Re\sum\nolimits^{\mathrm{GW}}_{n\mathbf{k}} - V^{xc}_{n\mathbf{k}}\right)\right]^2 + \left[\Im\sum\nolimits^{\mathrm{GW}}_{n\mathbf{k}}\right]^2\right]^{-1} \tag{14}$$

is Lorentzian and the spreading (full-width at half maximum, FWHM) defines the strength of the correlated interaction. A sharp spectral function defines a less correlated interaction, while a dwarf and spread defines a strong interaction.
One of the major challenges when dealing with 2D systems, is the finite length in one of the spatial direction. This introduces rapid variations in screening and as a result the integral quantities like exchange self-energies, BS kernel, total energy expression, etc. suffers $\mathbf{q} \to 0$ divergence problem due to the quasi-2D nature of Coulomb interaction. In order to compute those quantities properly, "random integration method" emerged as the most numerically accurate methodology [8–10]. These divergences can be solved by the state-of-the-art computational methodologies performed on high-performance CPUs. We explain this in the spirit of [8–10]: The numerical evaluation of the GW self-energy (Eqn. (7)) is a horrendous task. A fine sampling of the BZ would require an exorbitant computational cost since large grids of transferred momenta are always connected with the use of equally large grids of k points [9]. Therefore a preferable solution is to fix certain k-points grid and the integration is then performed over the BZ by using a large random grid of points to do the q -summation. These random points are chosen in such a way to cover the whole of the BZ. Quantitatively, rewriting the Coulombic integral as $\int d^3\mathbf{q}\left[\frac{f(\mathbf{q})}{|\mathbf{q}+\mathbf{G}|^2}\right]$, each of this kind of term appearing in static or dynamic self-energy (in GW or BSE-only for oscillators and occupation numbers) is integrated around each $\mathbf{q}$ over a small volume centered at $\mathbf{q}+\mathbf{G}$ whereas the rest of the integrand $f(\mathbf{q})$ remains almost constant. Computationally, this

small volume could be a box for planar geometry, cylinder for one-dimensional geometry and sphere for bulk. The height of the box should be equal to the either side distance between the periodic images done while using ground state or the density functional theory task. We particularly this divergence overcome situation for the diagonal matrix elements, the case with off-diagonal matrix elements is then straight forward: The diagonal matrix element of the exchange self-energy (Eqn. (1)) after assuming that the integral is a smooth function of momenta, can then be written as

$$\langle n\mathbf{k}\,|\textstyle\sum^{x}|\,n\mathbf{k}\rangle \approx \sum_{\mathbf{q_i}}\sum_{\mathbf{G}} F\left(\mathbf{q_i},\mathbf{G}\right)\int_{small_{BZ}(\mathbf{q_i})} d^3\mathbf{q}\frac{4\pi}{\left|\mathbf{q}+\mathbf{G}\right|^2} \tag{15}$$

This integral can now be evaluated using a Montecarlo method and the procedure is known in literature as random integration method. This way we see that the $\mathbf{q_i} \to 0$ divergence is also resolved here since the 3D $\mathbf{q}$ integration forbids this to happen. In addition, the integral pre-factor is also regular when $\mathbf{q_i} \to 0$. Some large random points can be incorporated in order to evaluate the Coulomb integrals with a $\mathbf{G}$-vector suitable cut-off. The numerical integral was defined within a box-structure extending some vacuum distance on either side of the monolayer. This truncates the Coulomb potential between the repeated images and a faster convergence can be achieved.

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