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Relationship between the random-phase approximation ground-state total energy and *GW* quasiparticle energy

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A connection between the random-phase-approximation (RPA) total energy E_{RPA} and the *GW* quasiparticle energy ϵ_{GW} has been pointed out. More specifically we show that: $\delta E_{\mathrm{RPA}}(N)/\delta N=\epsilon_{GW}$, where N is the total number of electron. The variational property of the RPA total energy is also discussed and the variational equations for the orbital wave functions are derived. We argue that the RPA formalism is a method which can provide both accurate ground-state energies and single quasiparticle energies.

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There is a recent resurgence of interest to use random-phase approximation (RPA) to calculate the electron correlation energies in solids and molecules.[1–7] This is driven by several factors: the lack of continuing progress in charge-density-based localized formalism to improve the density-functional theory; the realization that nonlocal functional is necessary to handle energies such as the van der Waals interactions; the increased computational power enabling the calculation of more complicated formalisms. The current local-density approximation (LDA) and generalized gradient approximation (GGA) formalisms suffers from several problems: (1) significant error in describing the molecular dissociation energy; (2) underestimation of the atomic diffusion barriers; (3) inability to describe the van der Waals interactions; and (4) underestimation of the band gaps for semiconductors and insulators. It is realized that to overcome these problems, a correlation energy expression-based on orbital wave functions might be necessary.[8] While the hybrid functionals[9] are developed empirically, there is a more rigorous approach to calculate the correlation energy-based on fluctuation-dissipation theorem. Under this theorem, the correlation energy is related to the imaginary part of the inverse dielectric function. When RPA is used to describe the dielectric function, one yields the RPA expression for the correlation energy

$$E_c=\int_o^{\infty}\frac{d\omega}{2\pi}\mathrm{Tr}\{\ln[1-\chi^0(i\omega)v]+\chi^0(i\omega)v\}. \tag{1}$$

Here $\chi^0(i\omega)$ is the independent-particle polarization function at imaginary frequency $i\omega$ and v is the Coulomb interaction $1/|\mathbf{r}-\mathbf{r}'|$. Both χ^0 and v should be considered as matrix of index $\mathbf{r}$ and $\mathbf{r}'$, and the Tr denotes the trace of the matrix. The above formula can be derived from many different ways.[5,6,10–14] Initially, the RPA formula was found to under estimates the short-range part of the correlation energy.[13,15] Nevertheless, recent studies indicated that the RPA provides much better bulk lattice constants and bulk/molecule atomic dissociation energies than the LDA and GGA.[1,16–18] It was also found that the RPA formalism gives satisfactory energy curves for the van der Waals interactions.[3,4,7,19]

So far, all the investigations have been focused on the accuracy of ground-state total energies and the resulting atomic geometries (lattice constants, van der Waals minimum distance, etc.). However, there is a long desire[8,20] to develop a beyond-LDA/GGA formalism which not only provides more accurate ground-state energies but also accurate quasiparticle energies (hence the electronic structures). The quasiparticle energy is often calculated by the *GW* method with satisfactory accuracy.[21–23] Thus, it will be nice to connect the RPA ground-state total energy with the *GW* single quasiparticle energy. Although *GW* self-energy term is well known to be related to the RPA total-energy formalism, it is surprising that the formal connection[24] between these two energies has never been pointed out explicitly in the literature. More specifically, as our first task, we will show that: $\delta E_{\mathrm{RPA}}[N]/\delta N=\epsilon^{GW}$, here N is the number of electron in the system. As a result, the RPA might be a method which gives both the accurate ground-state energies and the quasiparticle energies. The above formula is the counter part of Koopmans' theorem[25] for Hartree-Fock calculations and Janak's theorem for LDA calculations.[26]

An ideal theory for material science simulation should also be a variational theory, i.e., the self-consistent solution of the wave functions should be the variational minimum (or stationary point) of the total energy. It is the second task of this article to discuss the variational properties of the RPA formalism.

We now proceed with the proof for the relationship between RPA total energy and the *GW* quasiparticle energy. The RPA total energy can be expressed as

$$E_{\mathrm{RPA}}=\int\left[\sum_i\frac{-f_i}{2}\psi_i^*(r)\nabla^2\psi_i(r)+V_{ion}(r)\rho(r)\right]d^3r + \frac{1}{2}\int\frac{\rho(r)\rho(r')}{|r-r'|}d^3rd^3r'+E_{XC}^{\mathrm{RPA}} \tag{2}$$

and here $\{\psi_i(r)\}$ is a set of orthonormal single-particle wave functions, f_i is the occupation of ψ_i which is between 0 and 1, and $\rho(r)=\Sigma_i f_i|\psi_i(r)|^2$. The V_{ion} is the ionic potential due to the nuclei. The exchange and correlation energy of RPA can be written as

$$E_{XC}^{\mathrm{RPA}}=\int_o^{\infty}\frac{d\omega}{2\pi}\mathrm{Tr}\{\ln[1-\chi^0(i\omega)v]\}. \tag{3}$$

Within RPA, the $\chi^0(r,r',\omega)$ can be expressed as a product of the single-particle Green's function $G(r,r',\omega)$

$$\chi^0(r,r',\omega) = \frac{-i}{2\pi}\int_{-\infty}^{\infty} d\omega' G(r,r',\omega'+\omega)G(r,r',\omega') \quad (4)$$

here the ω is in the real axis and G will be approximated by the noninteraction Green's function G_s as

$$G_s(r,r',\omega) = \sum_i \left[\frac{f_i\psi_i(r)\psi_i^*(r')}{\omega-\epsilon_i-i\eta} + \frac{(1-f_i)\psi_i(r)\psi_i^*(r')}{\omega-\epsilon_i+i\eta} \right] \quad (5)$$

here η is a small positive number and $\{\psi_i\}$ are a complete orthonormal single-particle wave-function set. After a contour integral on the complex plane of ω' in Eq. (4), we have an explicit expression for χ^0 as

$$\chi^0(r,r',\omega) = \sum_{i,j} \psi_i(r)\psi_j^*(r)\psi_i^*(r')\psi_j(r') \times \left[\frac{f_j(1-f_i)}{\epsilon_j-\epsilon_i+\omega+i\eta} + \frac{f_i(1-f_j)}{\epsilon_i-\epsilon_j-\omega+i\eta} \right]. \quad (6)$$

Now, to take $\delta E_{\text{RPA}}[N]/\delta N$ is equivalent to change the occupation number f_k on one orbital k, thus $\delta E_{\text{RPA}}/\delta f_k$. If we assume $\{\psi_i,\epsilon_i\}$ are fixed while the δf_k is changing, we have

$$\frac{\partial E_{\text{RPA}}}{\partial f_k} = \int \left(-\frac{1}{2}\psi_k^*(r)\nabla^2\psi_k(r) + [V_{ion}(r)+V_H(r)]|\psi_k(r)|^2 \right) d^3r + \frac{\partial E_{XC}^{\text{RPA}}}{\partial f_k}. \quad (7)$$

Here $V_H(r)=\int\rho(r')/|r-r'|d^3r'$ is the Hartree potential. Before going on, we first notice that $\chi^0(r,r',\omega)=\chi^0(r',r,-\omega)$, as a result, the half axis integral in Eq. (3) can be expanded into a full axis integral from $-\infty$ to ∞.[10] Now, $\partial E_{XC}^{\text{RPA}}/\partial f_k$ can be expressed as $\partial E_{XC}^{\text{RPA}}/\partial\chi^0 \times \partial\chi^0/\partial f_k$. The matrix derivative to $\ln(1-\chi^0\nu)$ can be understood as the derivative to its Taylor expansion. As a result, we have

$$\frac{\partial E_{XC}^{\text{RPA}}}{\partial f_k} = \int_{-\infty}^{\infty} \frac{d\omega}{4\pi}\text{Tr}\left[\nu(1-\chi^0(i\omega)\nu)^{-1}\frac{\partial\chi^0(i\omega)}{\partial f_k} \right]. \quad (8)$$

Now, under RPA, $\nu[1-\chi^0(i\omega)\nu]^{-1}=\nu\epsilon^{-1}(i\omega)=W(r,r',i\omega)$ with W being the screened Coulomb interaction. Using Eqs. (5) and (6), it is straightforward to show that

$$\frac{\partial\chi^0(r,r',\omega)}{\partial f_k} = G_s(r',r,\epsilon_k-\omega)\psi_k(r)\psi_k^*(r') + G_s(r,r',\epsilon_k+\omega)\psi_k^*(r)\psi_k(r'). \quad (9)$$

Substitute this into Eq. (8), we have

$$\begin{aligned}\frac{\partial E_{XC}^{\text{RPA}}}{\partial f_k} &= \int_{-\infty}^{\infty}\frac{d\omega}{4\pi}\int W(r',r,i\omega)[G_s(r',r,\epsilon_k-i\omega)\psi_k(r)\psi_k^*(r') \\ &\quad + G_s(r,r',\epsilon_k+i\omega)\psi_k^*(r)\psi_k(r')]d^3rd^3r' \\ &= \int\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}W(r',r,i\omega)G_s(r',r,\epsilon_k - i\omega)\psi_k(r)\psi_k^*(r')d^3rd^3r' \\ &= \int \psi_k^*(r')\Sigma(r',r,\epsilon_k)\psi_k(r)d^3rd^3r' \end{aligned} \quad (10)$$

here we have used $W(r,r',\omega)=W(r',r,-\omega)$, which can be shown from $\nu(1-\chi^0\nu)^{-1}$. Σ is the *GW* self-energy term (an imaginary ω integral is used here although it can also be changed into an real ω integral). Combine Eq. (7) with Eq. (10), we see that $\partial E_{\text{RPA}}/\partial f_k$ is the *GW* quasiparticle energy ϵ_k^{GW} for orbital ψ_k. Note that this result is valid for both conduction bands and valence bands, and $\{\psi_i,\epsilon_i\}$ need not to be the solution of the *GW* equation, and ϵ_k does not need to equal ϵ_k^{GW}.

In the above derivation, we have assumed $\{\psi_i,\epsilon_i\}$ are fixed while f_k is changing. In reality, in a self-consistent procedure, $\{\psi_i,\epsilon_i\}$ might change when f_k is changed. In order for the above result to remain valid under such self-consistent calculation, we need $\{\psi_i,\epsilon_i\}$ to be the variational solution of E_{RPA} of Eq. (2) so that the additional change of E_{RPA} caused by the changes of ψ_i and ϵ_i (induced by the change of f_k) is zero. One way to carry out a variational calculation of RPA is via the optimized-effective-potential (OEP) method,[27] under which the $\{\psi_i,\epsilon_i\}$ are solutions of a Schrodinger's equation with a local potential $V_{\text{OEP}}(r)$, and the E_{RPA} is a minimum under the variational change of V_{OEP} (i.e., under the change in $\{\psi_i,\epsilon_i\}$ induced by the change in V_{OEP}). However, here we will discuss the variational property of RPA under the direct explicit change of $\{\psi_i,\epsilon_i\}$ with only the constraint that $\{\psi_i\}$ is an orthonormal complete set. This is more variational with less constraints on $\{\psi_i\}$ and $\{\epsilon_i\}$ compared with the OEP approach. We start with the Klein's functional,[6,28] which expresses the total energy as a functional of the fully flexible Green's function $G(r,r',\omega)$. The Klein's functional under RPA approximation is

$$E_K[G] = E_{XC}^{\text{RPA}}[G] + U_H[G] + \text{Tr}(1-G_0^{-1}G) - \text{Tr}[\ln(-G^{-1})] + \mu N. \quad (11)$$

Here, μ is the Fermi energy and N is the total number of electron. E_{XC}^{RPA} is the same as in Eq. (3), except that the χ^0 is expressed as GG as in Eq. (4). $U_H[G]=1/2\int\rho(r)\rho(r')/|r-r'|d^3rd^3r'$ is the Hartree energy, and $\rho(r)=\frac{1}{2\pi i}\int_{-\infty}^{\infty}G(r,r,iz+\mu)e^{iz\delta}dz$ (δ is a small positive number), $G_0^{-1}(\omega)=\omega+\nabla^2/2-V_{ion}$. We have used a matrix notation for index r and r'. All the terms except U_H have a vertical line ω integral at $\omega=iz+\mu$: $1/2\pi\int_{-\infty}^{\infty}dze^{iz\delta}$, we will call this contour Γ.

It has been shown that[6,28] when G is approximated by G_s in Eq. (5) and $f_i=1$ for valence band, $f_i=0$ for conduction band, then E_K of Eq. (11) equals E_{RPA} of Eq. (2). To prove this, one needs to show the last three terms in Eq. (11) equal the first two terms in Eq. (2). Using the ω contour integral (closed at left plane), it is straight forward to show

$$\text{Tr}(1-G_0^{-1}G_s) = \sum_{i\in v}\left[-\epsilon_i + \int \psi_i^*\left(-\frac{1}{2}\nabla^2+V_{ion}\right)\psi_i d^3r \right] \quad (12)$$

here v denotes the valence bands. Carrying out the trace integral directly, the second last term of Eq. (11) becomes

$$-\mathrm{Tr}[\ln(-G_s^{-1})] = \frac{-1}{2\pi i}\sum_i \int_{\infty}^{-\infty} \ln(-iz-\mu+\epsilon_i)e^{iz\delta}dz$$
$$= \sum_{i\in v}(\epsilon_i-\mu). \qquad (13)$$

The second line of this equation has been derived in Ref. 29 [see its Eq. (54) and its Appendix A]. Combine Eqs. (12) and (13), we see that $E_K(G_s)$ of Eq. (11) equals E_{RPA} of Eq. (2). Note that, this is true as long as G equals G_s described by $\{\psi_i,\epsilon_i\}$ in Eq. (5) but $\{\psi_i,\epsilon_i\}$ do not need to be any self-consistent solutions. Furthermore, in the following, we will only consider $f_i=1$ for valence band and $f_i=0$ for conduction band. Thus, $\{f_i\}$ will not change when $\{\psi_i,\epsilon_i\}$ change.

Now, we take a derivative of $E_K[G]$ respective to G. When this derivative is taken, we treat each G element $G(r,r',i\omega)$ as an independent variable. Thus, the derivative itself is also a matrix of index r,r' and parameter $i\omega$. We first note the following: $-\frac{\partial}{\partial G}\mathrm{Tr}[\ln(-G^{-1})]=G^{-1}$; $\frac{\partial}{\partial G}\mathrm{Tr}(1-G_0^{-1}G)=-G_0^{-1}$, $\frac{\partial}{\partial G}U_H=V_H$, $\frac{\partial}{\partial G}E_{XC}^{\mathrm{RPA}}[G]=\nu[1-\chi^0\nu]^{-1}\partial\chi^0/\partial G=WG=\Sigma$. Put these together, we have

$$\frac{\partial}{\partial G}E_K[G] = \left[-\omega-\frac{1}{2}\nabla^2+V_{ion}+V_H+\Sigma\right]+G^{-1}. \qquad (14)$$

Thus, $\partial E_K/\partial G=0$ is the Dyson's equation for the Green's function G. This is known in the original paper of Klein.[28] If we can get the full G which satisfies the Dyson's equation, then it gives the variational minimum (or stationary point) of E_K. Unfortunately, the Dyson's equation for the full Green's function $G(r,r',\omega)$ is computationally difficult to solve, and the noninteraction Green's function G_s of Eq. (5) cannot satisfy the Dyson equation regardless what ψ_i, ϵ_i are used, although it might be a good approximation of the full G. If we restrict ourselves to G_s (hence $\{\psi_i,\epsilon_i\}$), we then want to know what are the corresponding variational equations of E_{RPA} under the change of ψ_i and ϵ_i. Because $E_{\mathrm{RPA}}[G_s]=E_K[G_s]$, thus $\Delta E_{\mathrm{RPA}}=\Delta E_K=\mathrm{Tr}[(\partial E_K/\partial G)\Delta G_s]$. We first calculate $T=\mathrm{Tr}[(\partial E_K/\partial G)G_s']$, then take the derivative on G_s' later. We first replace $\{\psi_i,\epsilon_i\}$ with notation $\{\varphi_i,\lambda_i\}$ in the expression of G_s' while keep using $\{\psi_i,\epsilon_i\}$ in the expression for $(\partial E_K/\partial G)$, thus we can take the derivative later only on $\{\varphi_i,\lambda_i\}$. One can regard T as a measure of the error on the Dyson equation when G_s is used to replace the full G. Using Eq. (14), we now have

$$T = \mathrm{Tr}\left[\frac{\partial E_K}{\partial G}G_s'\right] = \frac{1}{2\pi i}\int_\Gamma d\omega\left[[-\omega+H_0+\Sigma(\omega)]+\sum_j(\omega-\epsilon_j)\psi_j(r)\psi_j^*(r')\right]$$
$$\times\sum_i\frac{\varphi_i(r')\varphi_i^*(r)}{\omega-\lambda_i}e^{\omega\delta}d^3r d^3r'$$
$$= \sum_i\left[\langle\varphi_i|H_i|\varphi_i\rangle - \sum_{i\in v,j}\epsilon_j\langle\psi_j|\varphi_i\rangle\langle\varphi_i|\psi_j\rangle\right]. \qquad (15)$$

Here $H_0=-1/2\nabla^2+V_{ion}+V_H$ and $H_i=H_0+\Sigma_c(\lambda_i)$ for $i\in v$ and $H_i=-\Sigma_v(\lambda_i)$ for $i\in c$ (conduction band). The Γ integral on ω has been carried out analytically using the GW expression for $\Sigma(\omega)$, and we have

$$\Sigma_{v(c)}(r,r',\omega) = \int_\infty^\infty\frac{d\omega'}{2\pi}W(r,r',i\omega')G_{v(c)}(r,r',\omega-i\omega') \qquad (16)$$

and

$$G_{v(c)}(r,r',\omega) = \sum_{i\in v(c)}\frac{\psi_i(r)\psi_i^*(r')}{\omega-\epsilon_i-i\eta_{v(c)}}, \qquad (17)$$

where $\eta_v>0$ and $\eta_c<0$. Thus, G_v and G_c are the first and second terms of G_s in Eq. (5), describing the hole and electron propagations, respectively, and $G_v(\omega)+G_c(\omega)=G_s(\omega)$. We will only concern about the real part of T. For this we can defined a Hermitianized H_i. We will use the notation $\bar{A}(r,r',\lambda)\equiv[A(r,r',\lambda)+A^*(r',r,\lambda)]/2$. Then to get $\mathrm{Re}(T)$, one can change H_i to $\bar{H}_i$ in Eq. (15). We will also use only real ϵ_i and λ_i. We now change $\{\varphi_i,\lambda_i\}$ from $\{\psi_i,\epsilon_i\}$ to $\{\Delta\psi_i+\psi_i,\Delta\epsilon_i+\epsilon_i\}$ and use the constraint that $\{\varphi_i\}$ is orthonormal, hence $\langle\Delta\psi_i|\psi_j\rangle=-\langle\psi_i|\Delta\psi_j\rangle$ and $\Delta E_{\mathrm{RPA}}=\Delta_{\varphi_i,\lambda_i}[\mathrm{Re}(T)]$, we then have

$$\Delta E_{\mathrm{RPA}} = \sum_{i,j}\langle\Delta\psi_i|\psi_j\rangle\langle\psi_j|(\bar{H}_i-\bar{H}_j)|\psi_i\rangle$$
$$+\sum_i\frac{\partial}{\partial\omega}\langle\psi_i|\bar{H}_i(\omega)|\psi_i\rangle|_{\epsilon_i}\Delta\epsilon_i. \qquad (18)$$

Note one can also get this equation by directly taking the derivative from Eq. (2). But the use of Eq. (14) helps us to connect our equations to the more general variational equation-based on full G. In some sense, the condition for $\Delta\,\mathrm{Re}(T)=0$ is to minimize the error on the Dyson's equation when G is restricted to G_s.

Now, in order for the E_{RPA} to be variationally stationary, we need every individual term in Eq. (18) to be zero, we thus have the following variational equations for the RPA total energy:

$$\langle\psi_j|[H_0+\bar{\Sigma}_c(\epsilon_i)+\bar{\Sigma}_v(\epsilon_j)]|\psi_i\rangle=0 \quad \text{for } j\in c, i\in v,$$

$$\langle\psi_j|[\bar{\Sigma}_{c(v)}(\epsilon_i)-\bar{\Sigma}_{c(v)}(\epsilon_j)]|\psi_i\rangle=0 \quad \text{for } i,j\in v(c),$$

$$\frac{\partial}{\partial\omega}\langle\psi_i|\bar{\Sigma}_{c(v)}(\omega)|\psi_i\rangle|_{\epsilon_i}=0 \quad \text{for } i\in v(c). \qquad (19)$$

In principle, this set of equation can be used to uniquely determine $\{\psi_i,\epsilon_i\}$ because the number of equations is the same as the number of unknown variables (mind that $\{\psi_i\}$ is a complete set, thus its degree of freedom is the same as the number of r points). Note that the first equation for $j\in c$, $i\in v$ resemble the GW wave-function equation, except that $\bar{\Sigma}_v(\epsilon_i)$ has been replaced by $\bar{\Sigma}_v(\epsilon_j)$. Since the GW quasiparticle wave functions $\{\psi_i^{GW}\}$ [which are the solutions of the GW equation $[H_0+\Sigma(\epsilon_i^{GW})]\psi_i^{GW}=\epsilon_i^{GW}\psi_i^{GW}$] are not orthonormal, one cannot expect $\{\psi_i\}$ to satisfy the exact GW equation. One should not use $\{\psi_i^{GW},\epsilon_i^{GW}\}$ in the G_s expression of Eq.

(5) either due to their lack of orthonormal condition. Thus, the above Eq. (19) is a way to ensure that $\{\psi_i\}$ can be orthonormal while satisfying equations close to the GW equations. For the $i,j \in v$ case, the equation can be rewritten as

$$\langle\psi_j|[H_0+\bar{\Sigma}_c(\epsilon_i)+\bar{\Sigma}_v(\epsilon_a)]|\psi_i\rangle = \langle\psi_j|[H_0+\bar{\Sigma}_c(\epsilon_j)+\bar{\Sigma}_v(\epsilon_a)]|\psi_i\rangle. \tag{20}$$

Here ϵ_a can be the energy at the center of ϵ_i and ϵ_j. A similar equation can be written for the $i,j \in c$ case. Thus, again both sides of Eq. (20) resemble the GW equation. If the $\Sigma(\omega)$ does not have the ω dependence (e.g., under static approximation), then all the above equations can be satisfied by $\{\psi_i^{GW}\}$ and in that case $\{\psi_i^{GW}\}$ is orthonormal. Another interesting fact is that the ϵ_i is not given by the expectation value of ψ_i on a single-particle Hamiltonian, instead it is determined by the last equation in Eq. (19). Note that this is reasonable as long as the resulting ϵ_i can be used to describe the dynamical properties of G_s properly. This will not affect our $\delta E_{\text{RPA}}[N]/\delta N=\epsilon_k^{GW}$ conclusion, since ϵ_i does not need to equal ϵ_i^{GW}.

It is still an unknown question for whether the exact solution of Eq. (19) will give a physically meaningful result of $\{\psi_i,\epsilon_i\}$, e.g., whether it will be close to $\{\psi_i^{GW},\epsilon_i^{GW}\}$. Future numerical tests can help to address this question. One alternative method is to force $\{\psi_i,\epsilon_i\}$ to be close to $\{\psi_i^{GW},\epsilon_i^{GW}\}$ (or its orthogonalized counterpart) while try to satisfy Eq. (19) to the maximum extent. Another commonly used and numerically more practical approach is to generate $\{\psi_i,\epsilon_i\}$ as the eigenstates and energies of a ω independent Hamiltonian H_s (e.g., LDA or GGA) which is close to the GW single-particle Hamiltonian. This is much like the OEP approach.[27] Under the exact OEP approach, by definition, the E_{RPA} is a minimum under variational change of V_{OEP}, thus the variational principle will be guaranteed. The question there is how close is V_{OEP} to V_{LDA} or V_{GGA}, and how close is the resulting $\{\psi_i,\epsilon_i\}$ to $\{\psi_i^{GW},\epsilon_i^{GW}\}$. Let us discuss here that if the exact V_{OEP} is not used, instead only V_{LDA} or V_{GGA}, and their corresponding self-consistent LDA or GGA $\{\psi_i,\epsilon_i\}$ are used (much like in many of today's non-self-consistent RPA calculations), how large could be the violation of the RPA variational principle. Under such a scheme, the change $\{\Delta\psi_i,\Delta\epsilon_i\}$ is determined from ΔH_s (e.g. caused by electron occupation change or atomic movements) via perturbation theory. If we further make the approximation $\bar{\Sigma}_{c(v)}(\epsilon_i)-\bar{\Sigma}_{c(v)}(\epsilon_j) =\frac{\partial}{\partial\omega}\Sigma_{c(v)}(\epsilon_a)(\epsilon_i-\epsilon_j)$, here $\epsilon_a=(\epsilon_i+\epsilon_j)/2$ (which is reasonable since most interstate rotations happen at small $|\epsilon_i-\epsilon_j|$), then derived from Eq. (18), we have

$$\Delta E_{\text{RPA}} = 2\,\text{Re}\left\{\sum_{i\in v,j\in c}\frac{\langle\psi_i|\Delta H_s|\psi_j\rangle}{\epsilon_i-\epsilon_j}\times\langle\psi_j|[H_0+\Sigma_c(\epsilon_i) + \Sigma_v(\epsilon_j)]|\psi_i\rangle\right\} + \sum_{i,j\in v}\langle\psi_i|\Delta H_s|\psi_j\rangle\langle\psi_j|\frac{\partial}{\partial\omega}\bar{\Sigma}_c(\epsilon_a)|\psi_i\rangle + \sum_{i,j\in c}\langle\psi_i|\Delta H_s|\psi_j\rangle\langle\psi_j|\frac{\partial}{\partial\omega}\bar{\Sigma}_v(\epsilon_a)|\psi_i\rangle. \tag{21}$$

There are good reasons to believe the terms in the above formula should be small, although not exactly zero. As discussed before, the error for the first term should be small if ψ_i is close to ψ_i^{GW}. As we known[22] ψ_i^{LDA} is often very close to ψ_i^{GW}, thus similarly, such wave function ψ_i should also be close to the eigenstate of $H_0+\Sigma_c(\epsilon_i)+\Sigma_v(\epsilon_j)$, and since $\langle\psi_j|\psi_i\rangle=0$, the first term in Eq. (21) should be small. For the second and third terms in Eq. (21), they both involve exchange integrals between conduction bands and valence bands [this can be seen by plugging in Eqs. (16) and (17)]. Such electron-hole exchange integral is usually very small [on the order of meV (Ref. 30)] for smooth $W(r,r',\omega)$. This is because the electron and hole wave functions can have different atomic characteristics, their product integrates to zero over an unit cell. Thus the main contribution is likely from the local-field effect of $W(r,r',\omega)$, which is usually an order of magnitude smaller than the main part of W.[22,31] Thus, overall, we expect the ΔE_{RPA} in Eq. (21) to be small, and the variational principle will be valid approximately. It is up for future numerical work to test how small the terms are in Eq. (21) and whether they can be ignored in practice.

The satisfaction of the variational principle will ensure that $\delta E_{\text{RPA}}[N]/\delta N=\epsilon_k^{GW}(N)$ is valid under self-consistent calculation. Note, for a sufficiently large system (e.g., bulk) this also means $E_{\text{RPA}}[N\pm 1]-E_{\text{RPA}}[N]=\pm\epsilon_k^{GW}(N)$. Finally, the variational principle also allows the calculation of atomic force using Hellmann-Feynman theorem as $F_R =\int\rho(r)\,\partial V_{ion}(r)/\partial R d^3r$, here R is used to denote the atom and its coordinates. The Klein's functional also provides a way to go beyond the current RPA formalism, e.g., to provide a more accurate treatment for short-range correlation effect, which can improve both the ground-state total energies[13,15] and the quasiparticle energies.[23]

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