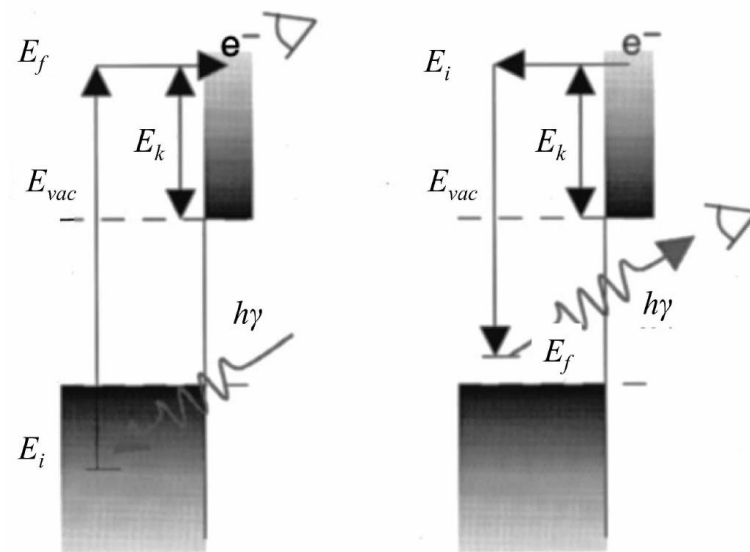
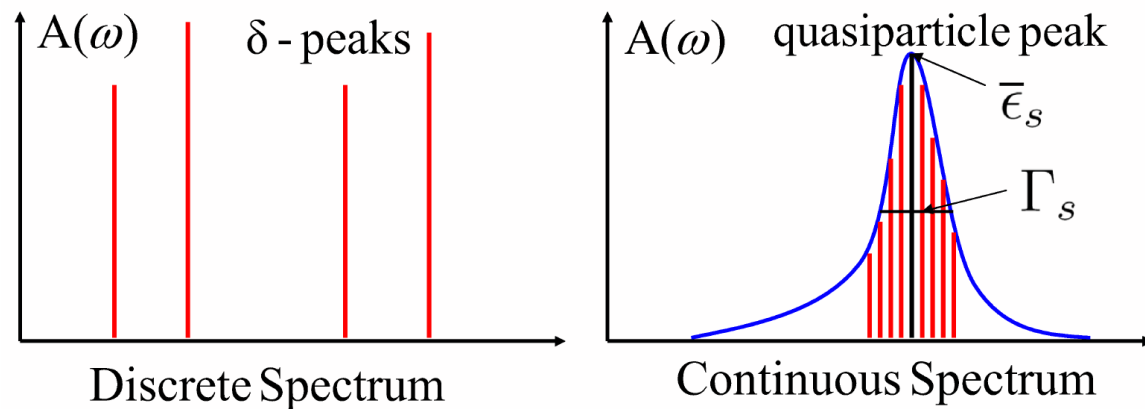


## $GW$ 近似

1. Lucia Reining, *The GW approximation: content, successes and limitations*, Advance Review 8, e1344 (2017)
2. F. Aryasetiawan and O. Gunnarsson, *The GW method*, Rep. Prog. Phys. 61, 237 (1998)
3. Hong Jiang, *The GW method: Theory and Implementation*, Manual, available on my homepage.
4. Xin-Zheng Li, *All-electron  $G_0W_0$  code based on FP-(L)APW+lo and applications*, Free-University Berlin, Ph.D thesis, June 05<sup>th</sup>, 2008.

# Motivation

1. 上节课最后，我们说到KS eigenvalue除了特殊态，并不对应严格的单粒子激发能。
2. 而单粒子激发谱对于凝聚态物理的研究是最基本的一个手段，前面均仁也讲到（准粒子激发），理论上将此性质描述清楚是理解后续物性（输运、光学性质）的基础。
3. 它所对应的物理过程如右图所示（PES, Inverse PES）：
4. 其中每个激发，对应的是一个谱，既有实部，也有虚部。实部对应激发能，虚部对应准粒子寿命，如下图：



5. 理论上，如果你是无相互作用量子系统，那你的单粒子激发谱很简单。有相互作用，很复杂。如何在理论上将类似过程描述清楚？就是我们这节课的任务。

# Motivation

这个Motivation的另外一种说法：

In Sec. 2.2.4, we pointed out that although the Kohn-Sham eigenvalues provide a good zeroth order approximation for the single particle excitation energies, LDA fails for a good description of the fundamental band gaps in semiconductors and insulations. On the other hand, many-body Green function theory provides the formal basis for evaluating the experimentally observed quasiparticle band structure. This chapter presents a short overview of the Green function method in the many-body electronic system, with a special emphasis on the  $GW$  approximation. This will set up the theoretical framework for our numerical implementation and the analysis of the results presented in this thesis.

# The Green Function

此方法中的关键函数：多电子系统中的单粒子格林函数

The single-particle Green function is defined as:

$$G(\mathbf{r}, t; \mathbf{r}', t') = -i \left\langle N \left| \hat{T} \left\{ \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right\} \right| N \right\rangle, \quad (4.1)$$

where  $\hat{\psi}(\mathbf{r}, t)$  and  $\hat{\psi}^\dagger(\mathbf{r}, t)$  are the quantum field operators describing the annihilation and creation of one electron at position  $\mathbf{r}$  and time  $t$ . The operator  $\hat{T}$  is the time-ordering operator, which reorders the field operators in ascending time order from right to left.  $|N\rangle$  is the groundstate eigenfunction of the  $N$  electrons system. Making use of the Heaviside function (Appendix J), and the commutation relations for Fermionic operators, Eq. 4.1 can be rewritten as:

$$\begin{aligned} G(\mathbf{r}, t; \mathbf{r}', t') = & -i \left\langle N \left| \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right| N \right\rangle \Theta(t - t') \\ & + i \left\langle N \left| \hat{\psi}^\dagger(\mathbf{r}', t') \hat{\psi}(\mathbf{r}, t) \right| N \right\rangle \Theta(t' - t). \end{aligned} \quad (4.2)$$

making evident that for  $t > t'$  ( $t < t'$ ) the Green function describes the propagation of an added electron (hole) in the system.

# The Green Function

In the Heisenberg representation, the field operator is written as:

$$\hat{\psi}(\mathbf{r}, t) = e^{i\hat{H}t} \hat{\psi}(\mathbf{r}) e^{-i\hat{H}t}, \quad (4.3)$$

where  $\hat{H}$  is the Hamiltonian operator and  $\hat{\psi}(\mathbf{r})$  is the field operator in the Schrödinger representation.

Inserting Eq. 4.3 into Eq. 4.2 and making use of the completeness relation in the Fock-space:

$$1 = \sum_{n=0}^{\infty} \sum_s |n, s\rangle \langle n, s|, \quad (4.4)$$

where  $|n, s\rangle$  corresponds to the  $s$ -th eigenstate of the the  $n$ -electron system, we can transform Eq. 4.2 into:

$$\begin{aligned} G(\mathbf{r}, t; \mathbf{r}', t') = & -i \sum_s \left\langle N \left| \hat{\psi}(\mathbf{r}) \right| N+1, s \right\rangle e^{-i(E_{N+1}^s - E_N)(t-t')} \\ & \cdot \left\langle N+1, s \left| \hat{\psi}^\dagger(\mathbf{r}') \right| N \right\rangle \Theta(t-t') + i \sum_s \left\langle N \left| \hat{\psi}^\dagger(\mathbf{r}') \right| N-1, s \right\rangle \\ & \cdot e^{-i(E_{N-1}^s - E_N)(t'-t)} \left\langle N-1, s \left| \hat{\psi}(\mathbf{r}) \right| N \right\rangle \Theta(t'-t). \end{aligned} \quad (4.5)$$

Here,  $E_N$  stands for the ground state energy of the  $N$ -electron system, and  $E_{N\pm 1}^s$  for the  $s$ -th excited state energy of the  $N \pm 1$  electronic system.

# The Green Function

Using the excitation energy  $\epsilon_s$  and amplitude  $\psi_s(\mathbf{r})$  defined by:

$$\begin{aligned} \epsilon_s &= E_{N+1}^s - E_N \quad , \quad \psi_s(\mathbf{r}) = \langle N | \hat{\psi}(\mathbf{r}) | N+1, s \rangle, \text{ for } \epsilon_s > \mu \\ \epsilon_s &= E_N - E_{N-1}^s \quad , \quad \psi_s(\mathbf{r}) = \langle N-1, s | \hat{\psi}(\mathbf{r}) | N \rangle, \text{ for } \epsilon_s \leq \mu, \end{aligned} \quad (4.6)$$

where  $\mu$  is the chemical potential of the  $N$ -electron system ( $\mu = E_{N+1} - E_N = E_N - E_{N-1} + O(N^{-1})$ ), we can further simplify Eq. 4.5 into the form:

$$\begin{aligned} G(\mathbf{r}, \mathbf{r}'; t - t') &= -i \sum_s \psi_s(\mathbf{r}) \psi_s^*(\mathbf{r}') e^{-i\epsilon_s(t-t')} \\ &\quad [\Theta(t - t') \Theta(\epsilon_s - \mu) - \Theta(t' - t) \Theta(\mu - \epsilon_s)]. \end{aligned} \quad (4.7)$$

Performing a Fourier transform to the frequency axis, we obtain the spectral, or Lehmann [85], representation:

$$G(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_s \psi_s(\mathbf{r}) \psi_s^*(\mathbf{r}') \left[ \frac{\Theta(\epsilon_s - \mu)}{\omega - (\epsilon_s - i\eta)} + \frac{\Theta(\mu - \epsilon_s)}{\omega - (\epsilon_s + i\eta)} \right]. \quad (4.8)$$

The key feature of Eq. 4.8 is that the Green function has single poles corresponding to the exact excitation energies of the many-body system. For excitation energies larger (smaller) than the chemical potential, these singularities lie slightly below (above) the real axis in the complex frequency plane (Fig. 4.1).

It can be easily shown that in the non-interacting case, Eq. 4.8, reduces to:

$$G_0(\mathbf{r}, \mathbf{r}', \omega) = \lim_{\eta \rightarrow 0^+} \sum_n \varphi_n(\mathbf{r}) \varphi_n^*(\mathbf{r}') \left[ \frac{\Theta(\epsilon_n - \epsilon_F)}{\omega - (\epsilon_n - i\eta)} + \frac{\Theta(\epsilon_F - \epsilon_n)}{\omega - (\epsilon_n + i\eta)} \right]. \quad (4.9)$$

where  $\epsilon_n(\varphi_n)$  is the eigenvalue (eigenfunction) of the single particle Hamiltonian and  $\epsilon_F$  is the Fermi energy.

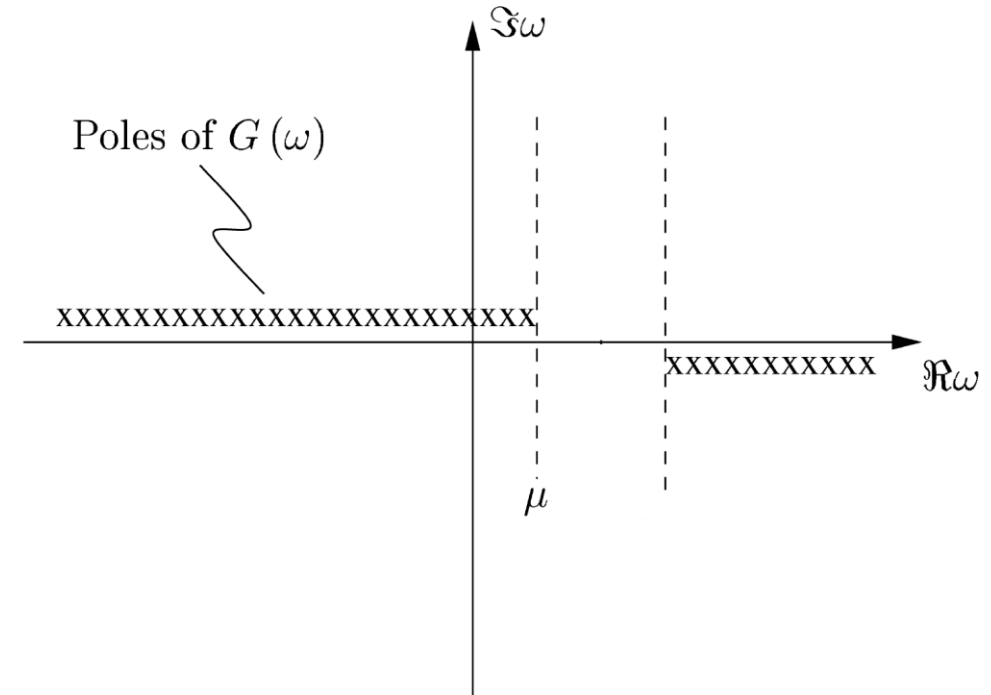


Figure 4.1: Position of the poles of the Green function (Eq. 4.8) in the complex frequency plane. Those corresponding to the unoccupied states are slightly below the real frequency axis while those corresponding to the occupied states are slightly above it.

# The Dyson Equation

The time evolution of the field operator, in the Heisenberg representation is given by the equation of motion:

$$i\frac{\partial}{\partial t}\hat{\psi}(\mathbf{r},t) = [\hat{\psi}(\mathbf{r},t), \hat{H}], \quad (4.10)$$

with the Hamiltonian operator given by:

$$\begin{aligned} \hat{H} = & \int d\mathbf{r} dt \hat{\psi}^\dagger(\mathbf{r},t) \left[ -\frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) \right] \hat{\psi}(\mathbf{r},t) \\ & + \frac{1}{2} \int \int d\mathbf{r} dt d\mathbf{r}' dt' \hat{\psi}^\dagger(\mathbf{r},t) \hat{\psi}^\dagger(\mathbf{r}',t') v(\mathbf{r},t; \mathbf{r}',t') \hat{\psi}(\mathbf{r}',t') \hat{\psi}(\mathbf{r},t), \end{aligned} \quad (4.11)$$

where  $v(\mathbf{r},t; \mathbf{r}',t') = \delta(t-t')/|\mathbf{r}-\mathbf{r}'|$  is the Coulomb interaction. By evaluating the commutator in Eq. 4.10, the equation of motion for the single particle Green function can be obtained:

$$\begin{aligned} & \left[ i\frac{\partial}{\partial t} + \frac{1}{2}\nabla^2 - V_{\text{ext}}(\mathbf{r}) \right] G(\mathbf{r},t; \mathbf{r}',t') \\ & + i \int d\mathbf{r}_1 \frac{1}{(\mathbf{r}-\mathbf{r}_1)} \langle N | T \left[ \hat{\psi}^\dagger(\mathbf{r}_1,t) \hat{\psi}(\mathbf{r}_1,t) \hat{\psi}(\mathbf{r},t) \hat{\psi}^\dagger(\mathbf{r}',t') \right] | N \rangle \\ & = \delta(\mathbf{r}-\mathbf{r}') \delta(t-t'), \end{aligned} \quad (4.12)$$

作业6

the quantity in the integrand of the second term is the two-particle Green function. Following the same procedure to obtain the equation of motion for the two-particle Green function will give a term depending on the three-particle Green function, and so on.

# The Dyson Equation

To break this hierarchy, the mass-operator is introduced, defined by:

$$\int d\mathbf{r}_1 dt_1 M(\mathbf{r}, t; \mathbf{r}_1, t_1) G(\mathbf{r}_1, t_1; \mathbf{r}', t') = \\ -i \int d\mathbf{r}_1 v(\mathbf{r} - \mathbf{r}_1) \langle N | T \left[ \hat{\psi}^\dagger(\mathbf{r}_1, t) \hat{\psi}(\mathbf{r}_1, t) \hat{\psi}(\mathbf{r}, t) \hat{\psi}^\dagger(\mathbf{r}', t') \right] | N \rangle. \quad (4.13)$$

Eq. 4.12 can then be rewritten:

$$\left[ i \frac{\partial}{\partial t} + \frac{1}{2} \nabla^2 - V_{\text{ext}}(\mathbf{r}) \right] G(\mathbf{r}, t; \mathbf{r}', t') - \int d\mathbf{r}_1 dt_1 M(\mathbf{r}, t; \mathbf{r}_1, t_1) G(\mathbf{r}_1, t_1; \mathbf{r}', t') \\ = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (4.14)$$

Since the Hartree interaction is a one-particle operator, it is usually separated from the mass operator  $M$  to define the self-energy,  $\Sigma = M - V_{\text{H}}$ . Replacing the mass-operator in Eq. 4.14 we arrive at:

$$\left[ i \frac{\partial}{\partial t} - H_0(\mathbf{r}) \right] G(\mathbf{r}, t; \mathbf{r}', t') - \int d\mathbf{r}_1 dt_1 \Sigma(\mathbf{r}, t; \mathbf{r}_1, t_1) G(\mathbf{r}_1, t_1; \mathbf{r}', t') \\ = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'), \quad (4.15)$$

where:

$$H_0(\mathbf{r}) = -\frac{1}{2} \nabla^2 + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}). \quad (4.16)$$

In the Hartree approximation Eq. 4.15 becomes:

$$\left[ i \frac{\partial}{\partial t} - H_0(\mathbf{r}) \right] G_0(\mathbf{r}, t; \mathbf{r}', t') = \delta(\mathbf{r} - \mathbf{r}') \delta(t - t'). \quad (4.17)$$



# The Self Energy: Hedin's equation

Multiplying Eq. 4.15 by  $G_0$  on the left and using the hermiticity of the single particle operator together with Eq. 4.17, and integrating, yields the well-known Dyson equation:

$$G(\mathbf{r}, t; \mathbf{r}', t') = G_0(\mathbf{r}, t; \mathbf{r}', t') + \iint d\mathbf{r}_1 dt_1 d\mathbf{r}_2 dt_2 G_0(\mathbf{r}, t; \mathbf{r}_2, t_2) \Sigma(\mathbf{r}_2, t_2; \mathbf{r}_1, t_1) G(\mathbf{r}_1, t_1; \mathbf{r}', t'). \quad (4.18)$$

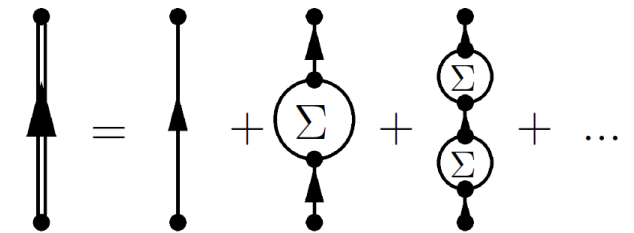
Recurrently replacing  $G$  on the right-hand side by  $G_0 + G_0 \Sigma G$ <sup>1</sup> leads to the series expansion:

$$G = G_0 + G_0 \Sigma G_0 + G_0 \Sigma G_0 \Sigma G_0 + \dots \quad (4.19)$$

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<sup>1</sup>In this symbolic notation, products imply an integration, as a product of matrices with continuous indices, *i. e.*  $AB = \int A(1, 3)B(3, 2)d3$

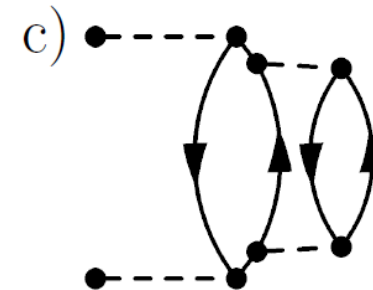
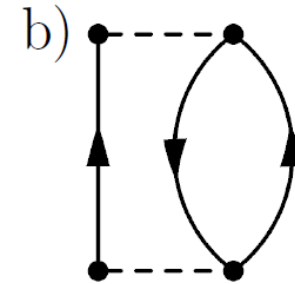
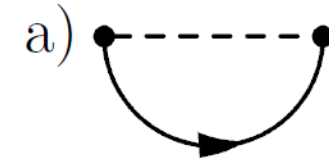
which shows that the single-particle propagator  $G(\mathbf{r}, t; \mathbf{r}', t')$  is equal to the “free” particle propagator  $G_0(\mathbf{r}, t; \mathbf{r}', t')$  plus the sum of the probability amplitudes of propagating from  $(\mathbf{r}, t)$  to  $\mathbf{r}', t'$  after single, double, etc.. scattering processes, with  $\Sigma$  playing the role of the scattering potential. Diagrammatically, this relation is shown as:



where the double plain arrow represents the interacting Green function, the plain arrow represents the non-interacting one.

# The Self Energy: Hedin's equation

For an electron propagating in a solid or molecule, the origin of the scattering processes lies in the Coulomb interaction with the Fermi sea. Thus, it is natural to expand the self-energy in terms of the bare Coulomb interaction. In the diagrams below, we show examples of some simple (low order) scattering processes. Diagram (a) is a first order scattering process that describes the propagating electron exchanging instantaneously, via the Coulomb interaction, its position with one electron from the Fermi sea. It corresponds to the exchange interaction. Solving the Dyson equation (4.15) including only this term in the self-energy and updating the Green function self-consistently yields the Hartree-Fock approximation. In diagram (b) the interaction of the probe electron with the Fermi sea excites an electron out of it, generating an electron-hole pair, which annihilate each other at a later time, interacting again with the probe electron. This second order scattering process, called “bubble” diagram, represents an electron repelling another from its neighborhood, thus generating a positive charge cloud around it. It is the simplest dynamical screening processes. In diagram (c), the excited electron in the electron-hole pair of diagram (b) further excites another electron-hole pair from the Fermi sea, changing the positive charge cloud around the probe electron again. Nevertheless, the long-range of the bare Coulomb interaction results in a poor convergence of this expansion for the self-energy, in fact, it diverges for metals.



# The Self Energy: Hedin's equation

In 1965, L. Hedin [8] proposed a different approach for obtaining the self-energy, by expanding it in terms of a dynamically screened Coulomb potential instead of the bare one. The derivation using the functional derivative technique can be found in Ref. [8, 86, 87]. Here, we just present the resulting set of equations:

$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) \quad (4.20a)$$

$$P(1, 2) = -i \int G(2, 3) G(4, 2) \Gamma(3, 4, 1) d(3, 4) \quad (4.20b)$$

$$W(1, 2) = v(1, 2) + \int W(1, 3) P(3, 4) v(4, 2) d(3, 4) \quad (4.20c)$$

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3^+) W(1, 4) \Gamma(3, 2, 4). \quad (4.20d)$$

where we used  $1 = (\mathbf{r}_1, t_1)$  to simplify the notation.  $\Gamma$  is a vertex function,  $P$  the polarizability and  $W$  the dynamically screened Coulomb potential. In Eq. 4.20a the vertex function is written in terms of a four point kernel (given by the functional derivative of the self-energy). Replacing the self-energy by the expression in Eq. 4.20d would allow to expand the vertex function in terms of the screened Coulomb potential. For the aim of this thesis, it will nevertheless be sufficient to represent it by a filled triangle:



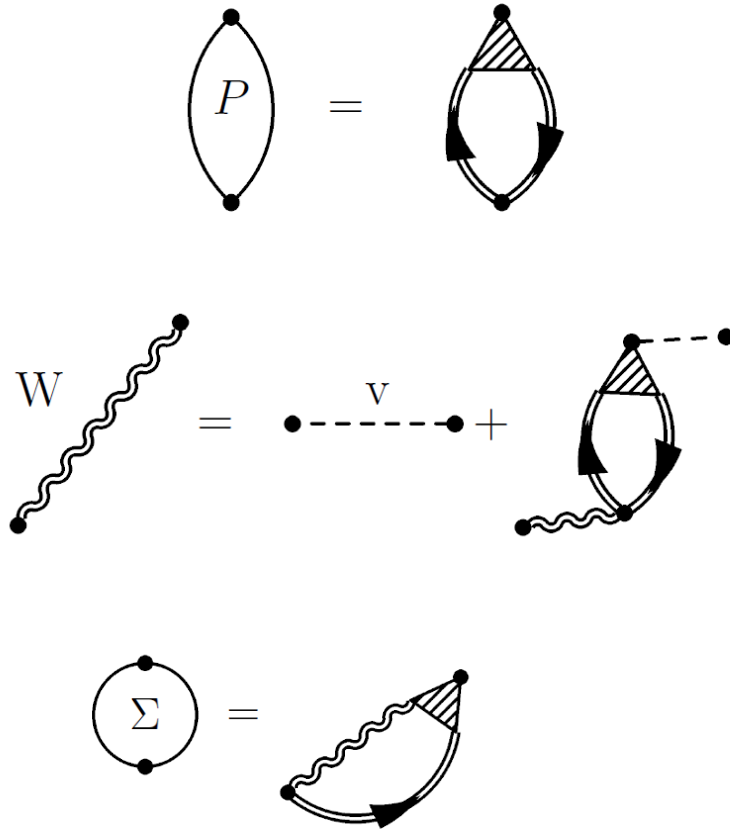
[8] L. Hedin, Phys. Rev. **139**, A796 (1965).

[86] L. Hedin and S. Lundqvist, Solid State Phys.: Advances in Research and Applications **23**, 1 (1969).

[87] F. Aryasetiawan and O. Gunnarsson, Rep. Prog. Phys. **61**, 237 (1998).

# The Self Energy: Hedin's equation

Eq. 4.20b, 4.20c, and 4.20d can then be represented diagrammatically as:



and

where the double wiggly line represents the screened Coulomb potential.

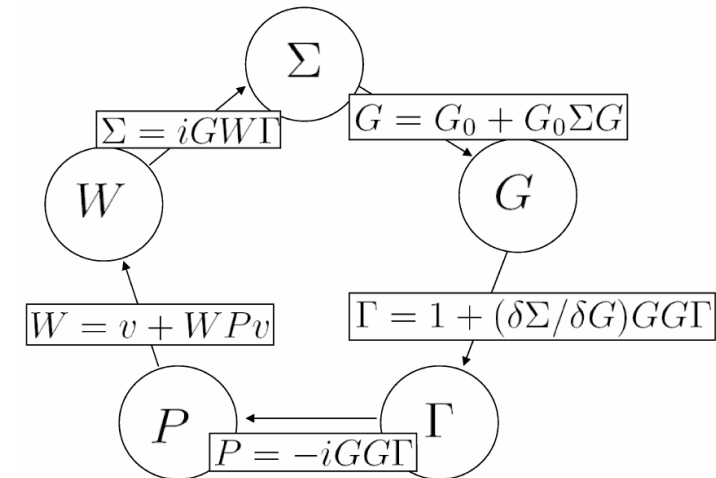
$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) \quad (4.20a)$$

$$P(1, 2) = -i \int G(2, 3) G(4, 2) \Gamma(3, 4, 1) d(3, 4) \quad (4.20b)$$

$$W(1, 2) = v(1, 2) + \int W(1, 3) P(3, 4) v(4, 2) d(3, 4) \quad (4.20c)$$

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3^+) W(1, 4) \Gamma(3, 2, 4). \quad (4.20d)$$

The set of equations 4.20, together with the Dyson equation (4.18), constitute the definitive solution of the quantum mechanical many-body problem. One just needs to solve them self-consistently to obtain the single-particle Green function of the interacting system (see Fig. 4.2). However, a direct numerical solution is prevented by the functional derivative in Eq. 4.20a, and, as usual, one has to rely on approximations. This will be the subject of the second part of this chapter.



# The Self Energy: $GW$ approximation

$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) \quad (4.20a)$$

$$P(1, 2) = -i \int G(2, 3) G(4, 2) \Gamma(3, 4, 1) d(3, 4) \quad (4.20b)$$

$$W(1, 2) = v(1, 2) + \int W(1, 3) P(3, 4) v(4, 2) d(3, 4) \quad (4.20c)$$

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3^+) W(1, 4) \Gamma(3, 2, 4). \quad (4.20d)$$



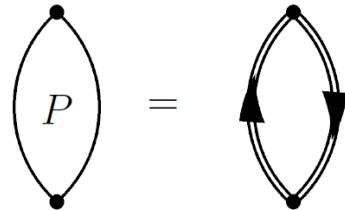
$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) \quad (4.25a)$$

$$P(1, 2) = -i G(1, 2) G(2, 1), \quad (4.25b)$$

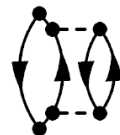
$$W(1, 2) = v(1, 2) + \int d(3, 4) W(1, 3) P(3, 4) v(4, 2), \quad (4.25c)$$

$$\Sigma(1, 2) = i G(1, 2) W(1^+, 2). \quad (4.25d)$$

Diagrammatically, the three-point  $\Gamma$  function is collapsed into a point. The elementary unit in this set of equations is the bubble diagram of the polarizability operator:



This approximation for the polarizability is known as the random-phase approximation (RPA). Physically, it represents the polarization generated by the creation and annihilation of a dressed electron-hole pair, while the interaction between the (dressed) electron and hole is neglected. In other words, scattering processes where the electron or the hole in the electron-hole pair interact with the medium are taken into account. For example, the process represented by the following diagram:

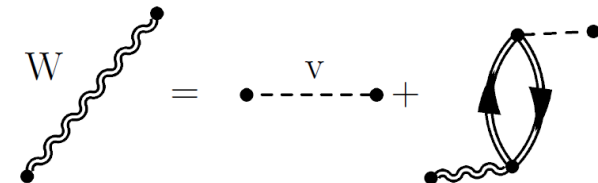


can be included. However, processes like:



where the electron and the hole interact with each other are neglected.

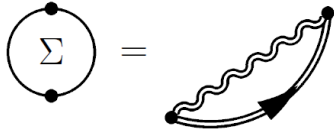
The screened Coulomb interaction resulting from Eq. 4.25c is the same as in Eq. 4.20c:



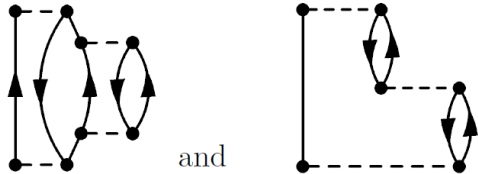
Except that now the polarizability is represented in the RPA.

# The Self Energy: $GW$ approximation

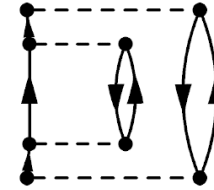
In Eq. 4.25d, the self-energy is written as a product of the Green function and the screened Coulomb interaction, diagrammatically:



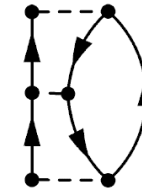
The shape of this diagram is similar to the Hartree-Fock approximation, with the instantaneous bare Coulomb potential replaced by the dynamically screened Coulomb one. This approximation to the self-energy includes processes represented, for example, by the diagrams:



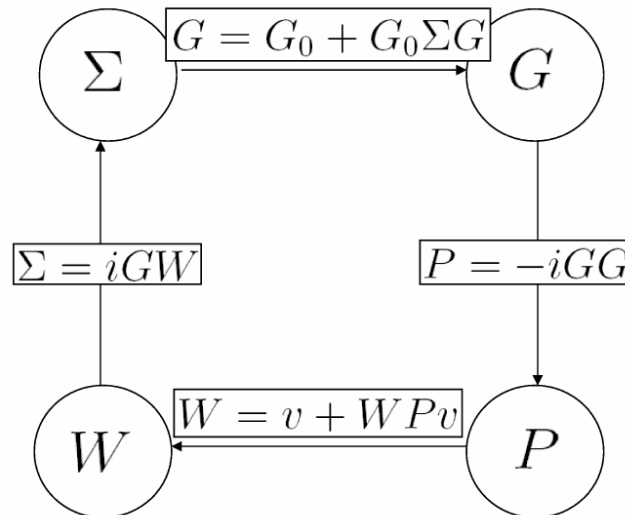
etc. through the screened Coulomb potential. Also processes like:



are included through the interacting Green function. However, diagrams like:



where the added electron interacts with that of the electron hole pair, are neglected.





# The $G_0 W_0$ method

Assuming one counts on an effective single-particle potential  $V^{\text{xc}}(\mathbf{r})$ , which contains some of the exchange-correlation effects in a many-body system and approximates reasonably well the self-energy, *i. e.*, the solutions of the single particle equation,

$$\hat{H}_{\text{eff}}(\mathbf{r})\varphi_i(\mathbf{r}) = \epsilon_i\varphi_i(\mathbf{r}) \quad (4.26)$$

with

$$\hat{H}_{\text{eff}}(\mathbf{r}) = \frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r}) \quad (4.27)$$

are such that  $\varphi_i(\mathbf{r}) \approx \psi_s(\mathbf{r})$  and  $\epsilon_i \approx \Re(\epsilon_s)$  ( $\psi_s(\mathbf{r})$  and  $\epsilon_s$  are the solutions of Eq. 4.23). The quasiparticle equation (4.23) can be rewritten,

$$\left[ \frac{1}{2}\nabla^2 + V_{\text{ext}}(\mathbf{r}) + V^{\text{H}}(\mathbf{r}) + V^{\text{xc}}(\mathbf{r}) \right] \psi_s(\mathbf{r}) + \int d\mathbf{r}' \Delta\Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_s) \psi_s(\mathbf{r}') = \epsilon_s \psi_s(\mathbf{r}) \quad (4.28)$$

where

$$\Delta\Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_s) = \Sigma(\mathbf{r}, \mathbf{r}'; \epsilon_s) - V^{\text{xc}}(\mathbf{r}') \delta(\mathbf{r} - \mathbf{r}'). \quad (4.29)$$

Since, according to our assumptions, the correction due to  $\Delta\Sigma$  are small, one can obtain the quasiparticle energies applying first order perturbation theory;

$$\begin{aligned} \psi_i(\mathbf{r}) &= \varphi_i(\mathbf{r}) \\ \epsilon_i^{\text{qp}} &= \epsilon_i + \langle \varphi_i(\mathbf{r}_1) | \Re[\Delta\Sigma(\mathbf{r}_1, \mathbf{r}_2; \epsilon_i^{\text{qp}})] \varphi_i(\mathbf{r}_2) \rangle. \end{aligned} \quad (4.30)$$

Taking the self-energy in the  $GW$  approximation, and further assuming that the non-interacting Green function  $G_0$  corresponding to  $\hat{H}_{\text{eff}}$  is a good approximation to the interacting one, the self-energy can be calculated through:

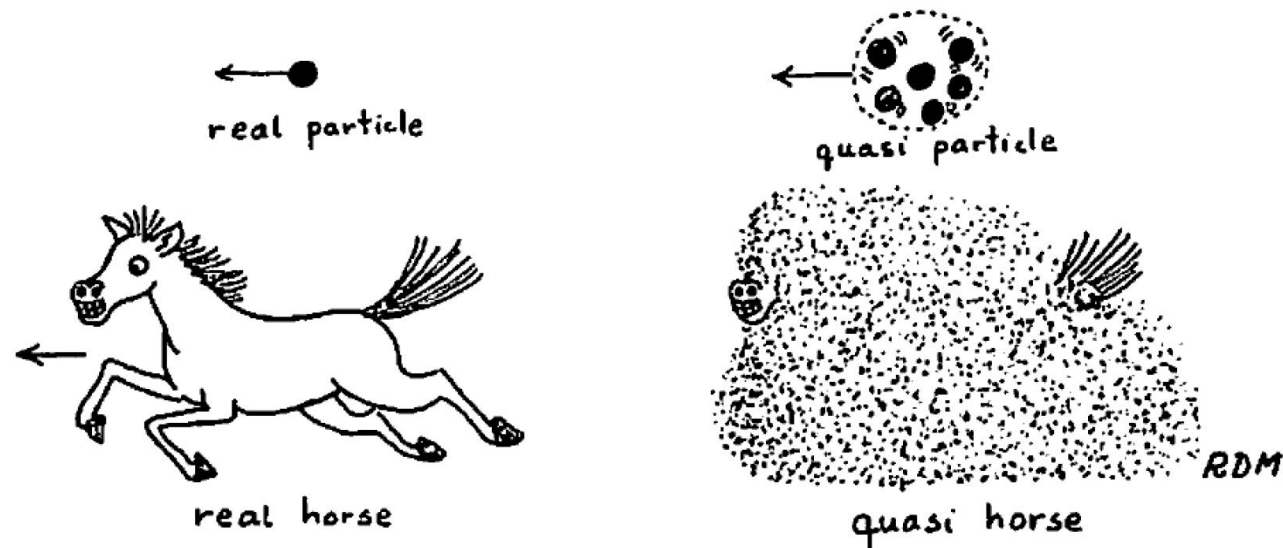
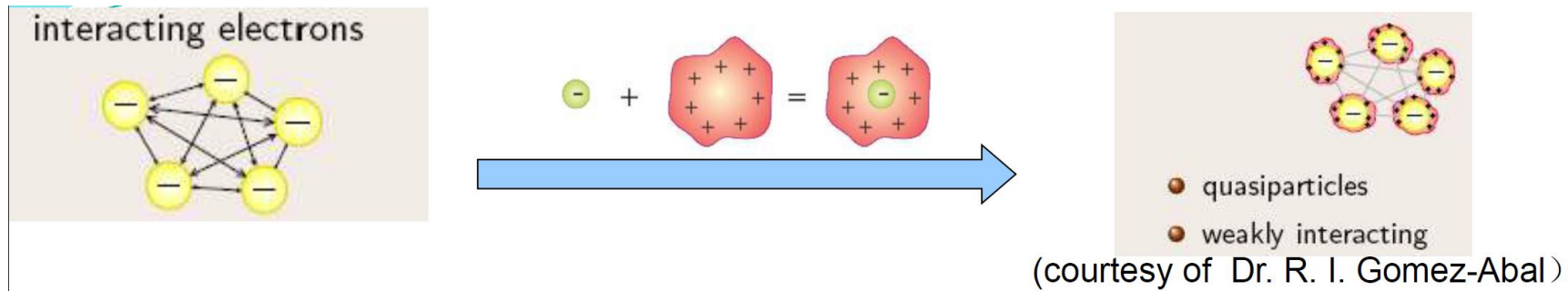
$$P_0(1, 2) = -iG_0(1, 2)G_0(2, 1), \quad (4.31a)$$

$$W_0(1, 2) = v(1, 2) + \int d(3, 4) W_0(1, 3) P(3, 4) v(4, 2), \quad (4.31b)$$

$$\Sigma(1, 2) = iG_0(1, 2)W_0(1^+, 2). \quad (4.31c)$$

usually known as the  $G_0W_0$  approximation.

# $GW$ versus HF



$$\left[ -\frac{\nabla^2}{2} + V_{\text{ext}}(\mathbf{r}) + V_{\text{H}}(\mathbf{r}) \right] \Psi_{n\mathbf{k}}(\mathbf{r}) + \int d^3\mathbf{r}' \Sigma_{\text{xc}}(\mathbf{r}, \mathbf{r}'; E_{n\mathbf{k}}) \Psi_{n\mathbf{k}}(\mathbf{r}') = E_{n\mathbf{k}} \Psi_{n\mathbf{k}}(\mathbf{r})$$

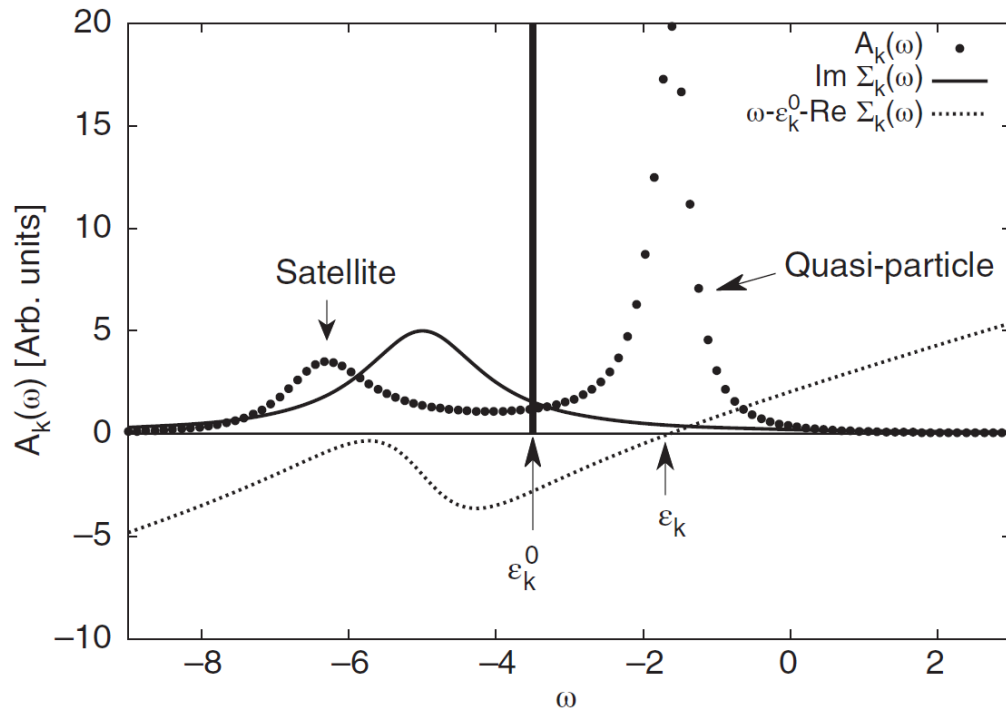


# $GW$ versus HF

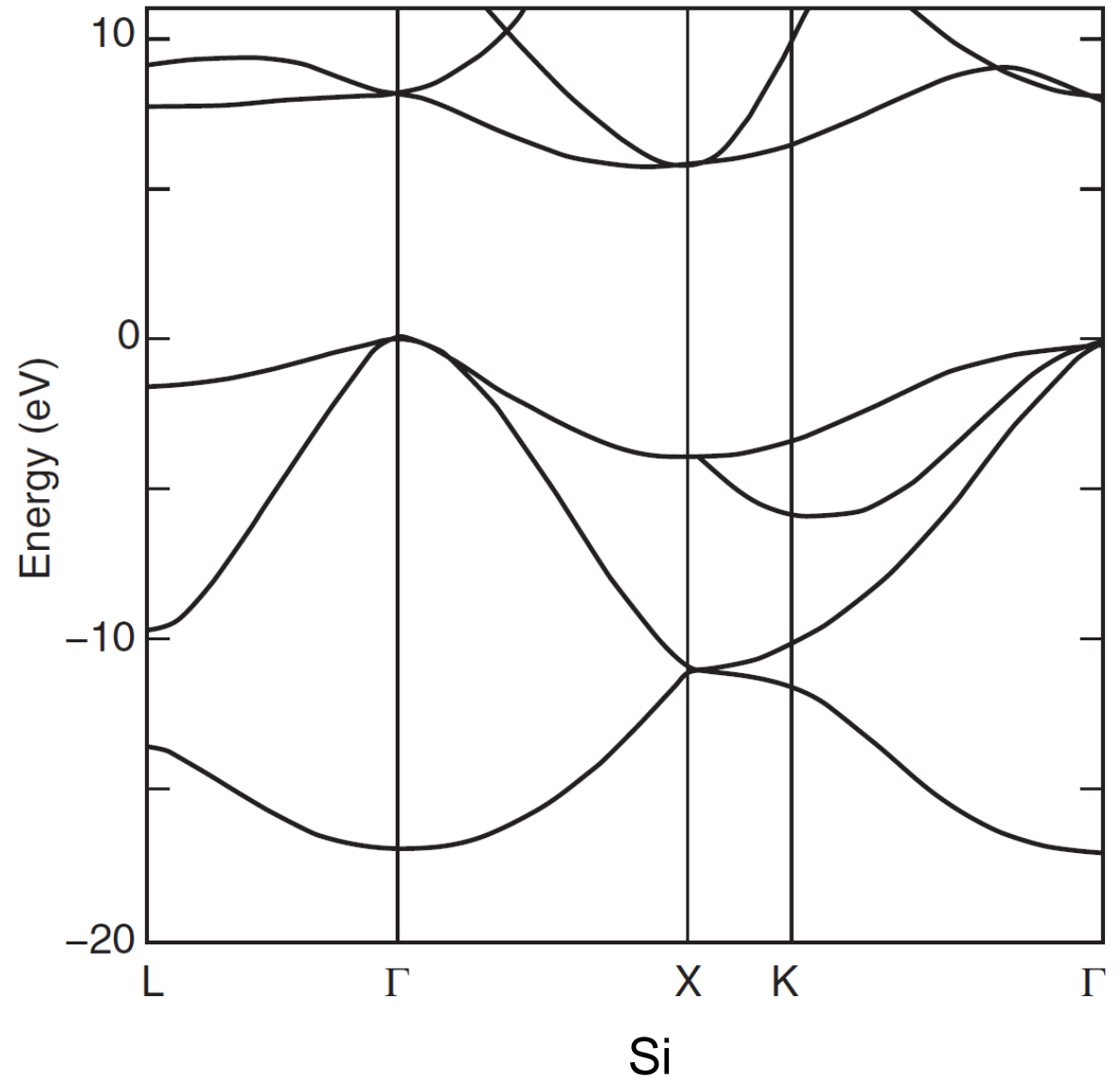


**FIGURE 10** | Pictorial representation of the Hartree–Fock (left panel) and GW (right panel) approximations. Hartree–Fock eigenvalues reflect electron addition or removal with respect to a rigid system, in the GW approximation the system responds dynamically. (Credits to Andrea Cucca, 2017).

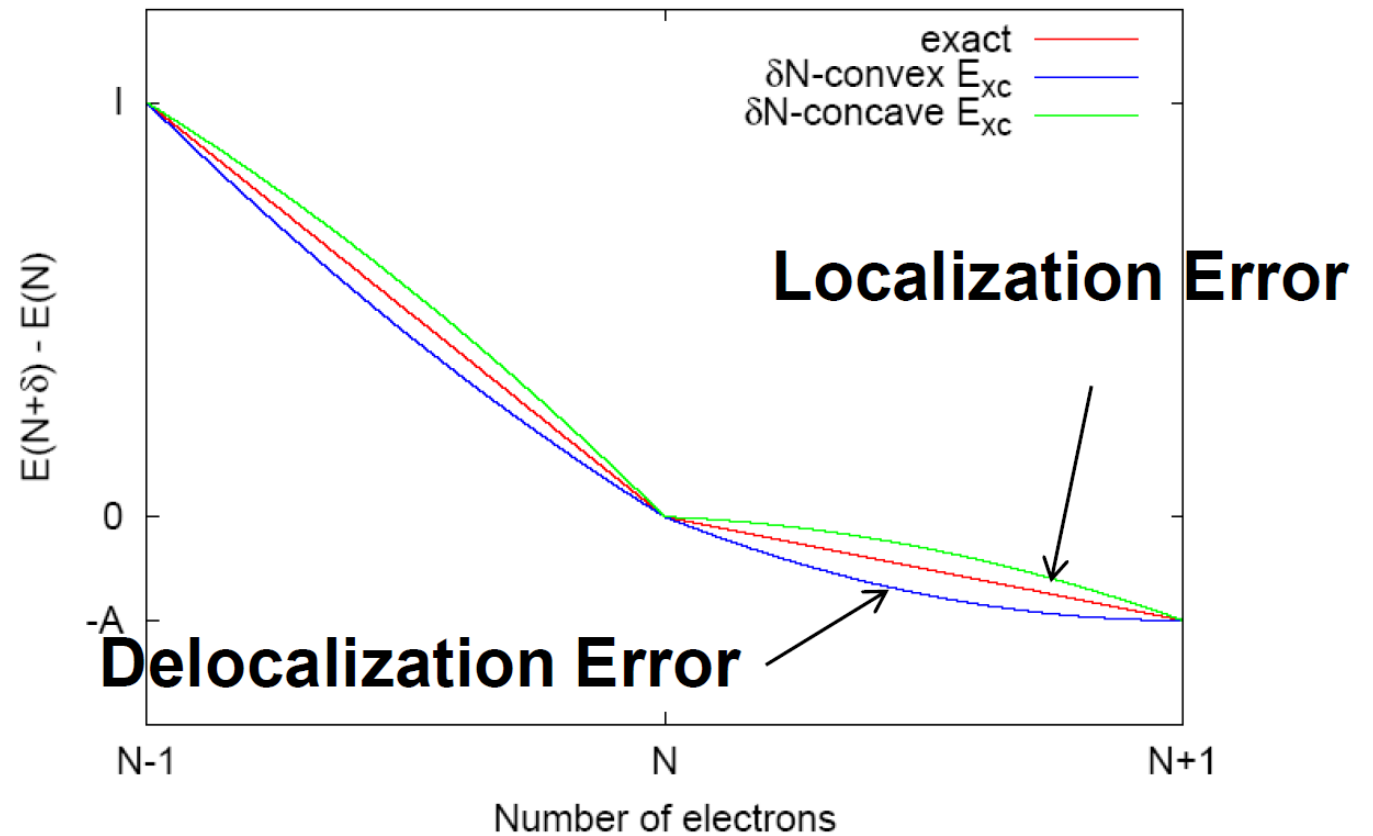
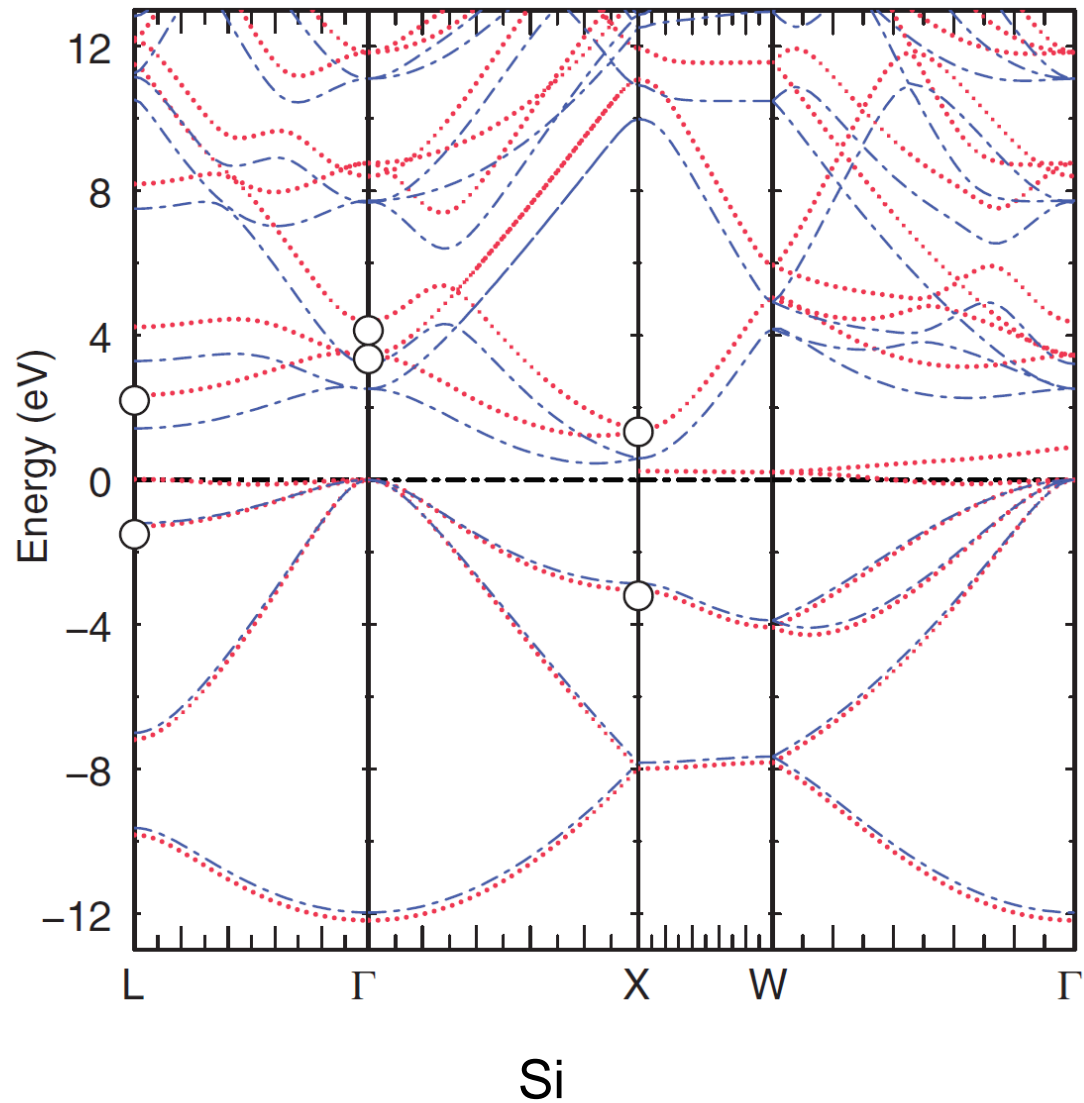
# *GW* versus HF



**FIGURE 2** | Typical electron removal spectral function matrix element in an extended system. The vertical line indicates an independent-particle result such as HF: it consists of one sharp peak. The interacting spectral function, given by the fat dots, exhibits a broad quasi-particle peak and a satellite due to excitations of the many-body system. Shown are also the imaginary (continuous line) and shifted real (dotted line) parts of the self-energy. The quasi-particle peak appears where the shifted real part crosses zero. Relative shifts would be different if another independent-particle system was chosen.



# $GW$ versus LDA、GGA



Aron J. Cohen, Paula Mori-Sanchez, and Weitao Yang,  
*Challenges for Density-Functional Theory*, Chem. Rev.  
112, 289 (2012)

# Flowchart of a $GW$ code

$$\epsilon_{n,\mathbf{k}}^{\text{qp}} = \epsilon_{n,\mathbf{k}} + \langle \varphi_{n,\mathbf{k}}(\mathbf{r}_1) | \Re [\Sigma(\mathbf{r}_1, \mathbf{r}_2; \epsilon_{n,\mathbf{k}}^{\text{qp}})] - V^{\text{xc}}(\mathbf{r}_1) \delta(\mathbf{r}_1 - \mathbf{r}_2) | \varphi_{n,\mathbf{k}}(\mathbf{r}_2) \rangle, \quad (5.1)$$

$$\Sigma(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') W_0(\mathbf{r}_2, \mathbf{r}_1; \omega') d\omega', \quad (5.2)$$

$$G_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \sum_{n,\mathbf{k}} \frac{\varphi_{n,\mathbf{k}}(\mathbf{r}_1) \varphi_{n,\mathbf{k}}^*(\mathbf{r}_2)}{\omega - \epsilon_{n,\mathbf{k}} \pm i\eta} \quad (5.3)$$

The self-energy can be separated into the exchange and correlation terms. If we define:

$$W_0^c(\mathbf{r}_1, \mathbf{r}_2; \omega) = W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) - v(\mathbf{r}_1, \mathbf{r}_2), \quad (5.7)$$

$$W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int \varepsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega) v(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3. \quad (5.4) \quad \text{where } v(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|} \text{ is the bare Coulomb potential, the exchange and correlation term of the self-energy can be calculated from:}$$

$$\varepsilon(\mathbf{r}_1, \mathbf{r}_2; \omega) = 1 - \int v(\mathbf{r}_1, \mathbf{r}_3) P(\mathbf{r}_3, \mathbf{r}_2; \omega) d\mathbf{r}_3, \quad (5.5)$$

$$P(\mathbf{r}_1, \mathbf{r}_2; \omega) = -\frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') G_0(\mathbf{r}_2, \mathbf{r}_1; \omega') d\omega' \quad (5.6)$$

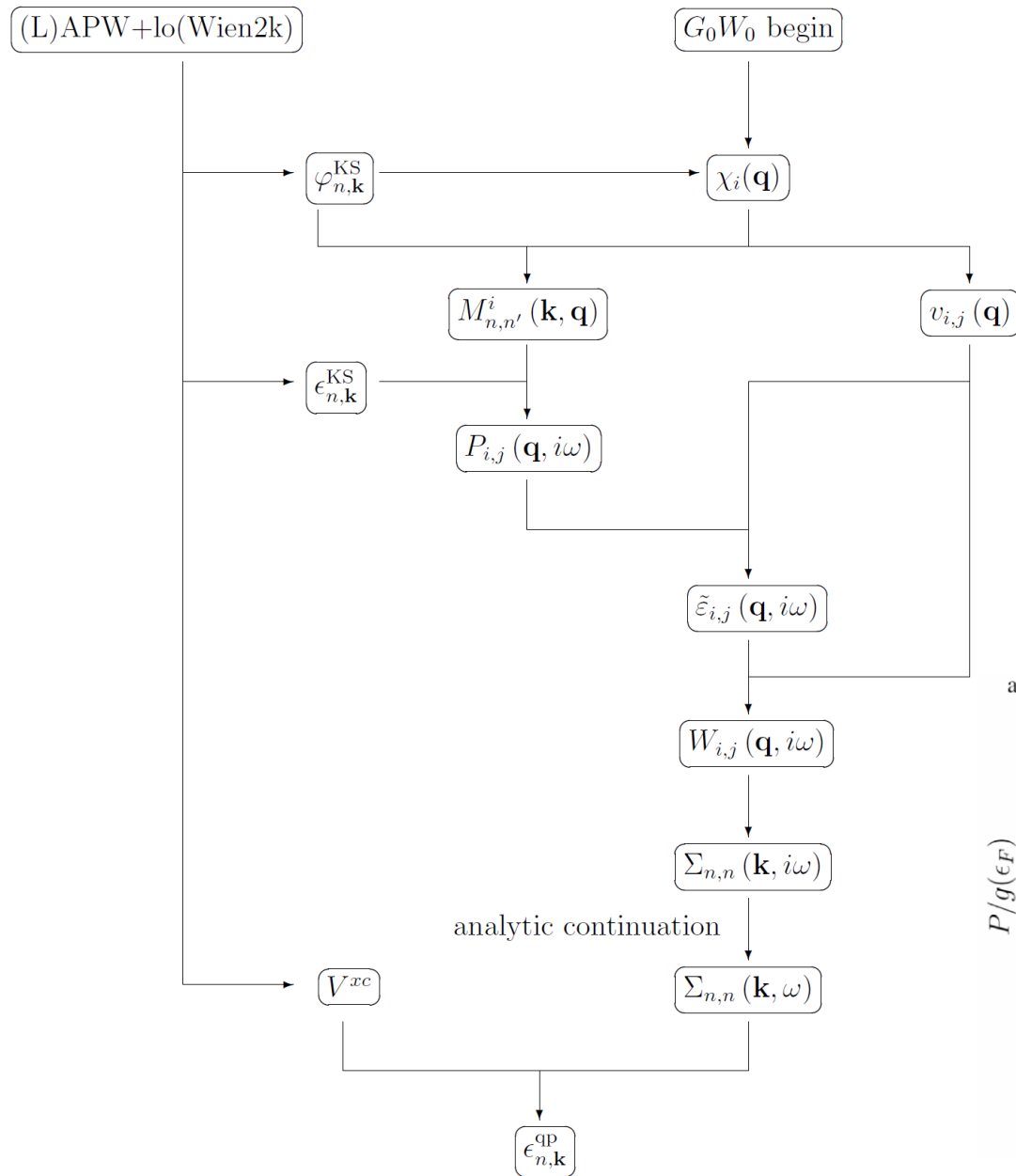
$$\begin{aligned} \Sigma^x(\mathbf{r}_1, \mathbf{r}_2) &= \frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega') v(\mathbf{r}_2, \mathbf{r}_1) d\omega' \\ &= \sum_{n,\mathbf{k}}^{\text{occ}} \varphi_{n,\mathbf{k}}(\mathbf{r}_1) v(\mathbf{r}_2, \mathbf{r}_1) \varphi_{n,\mathbf{k}}^*(\mathbf{r}_2) \end{aligned} \quad (5.8)$$

and

$$\Sigma^c(\mathbf{r}_1, \mathbf{r}_2; \omega) = \frac{i}{2\pi} \int G_0(\mathbf{r}_1, \mathbf{r}_2; \omega + \omega') W_0^c(\mathbf{r}_2, \mathbf{r}_1; \omega') d\omega' \quad (5.9)$$

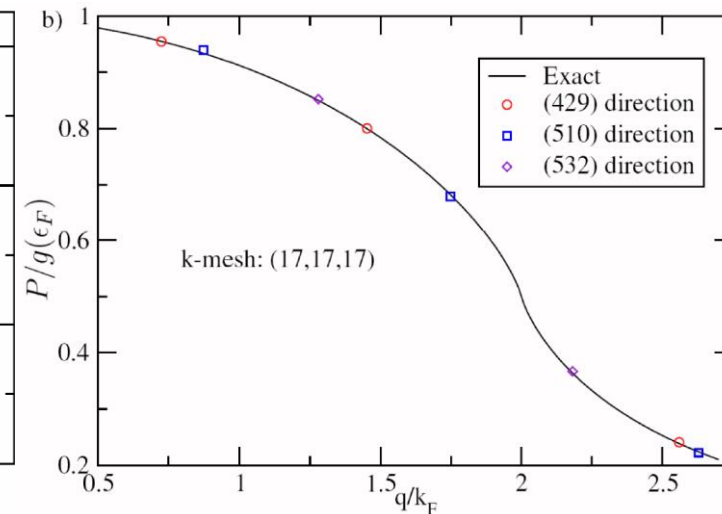
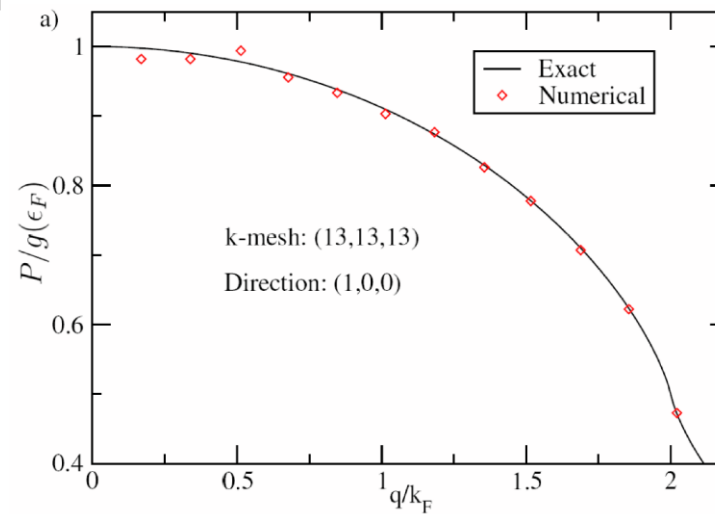
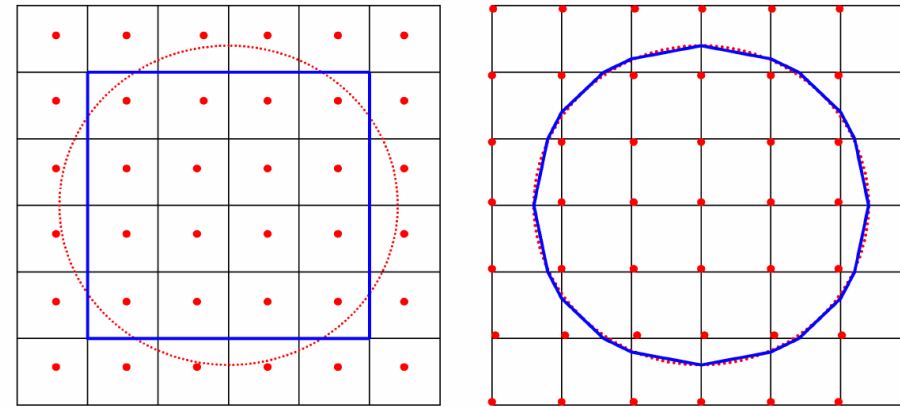
separately.

# Flowchart of a $GW$ code



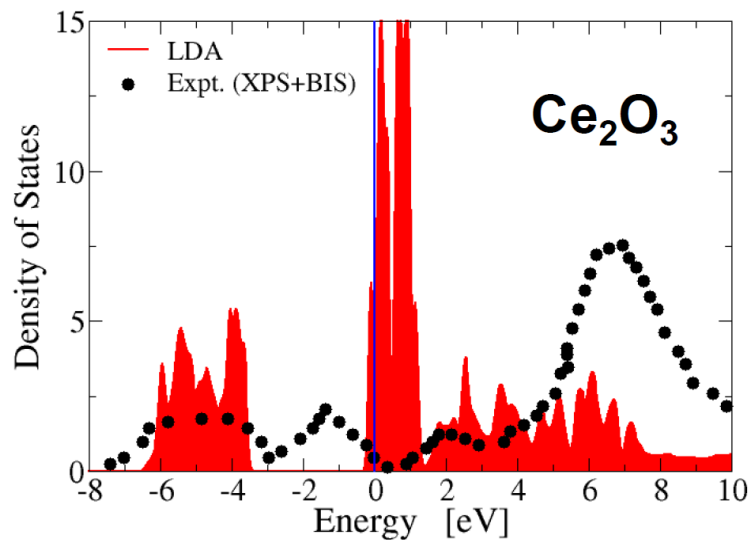
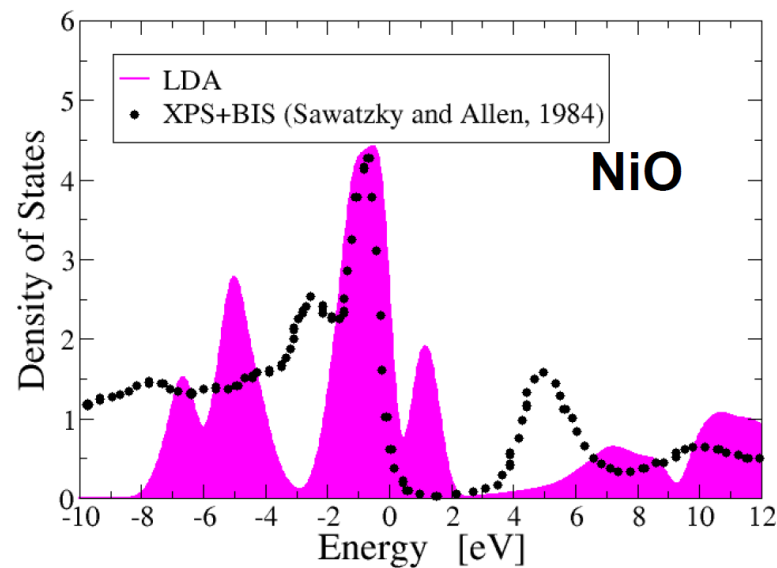
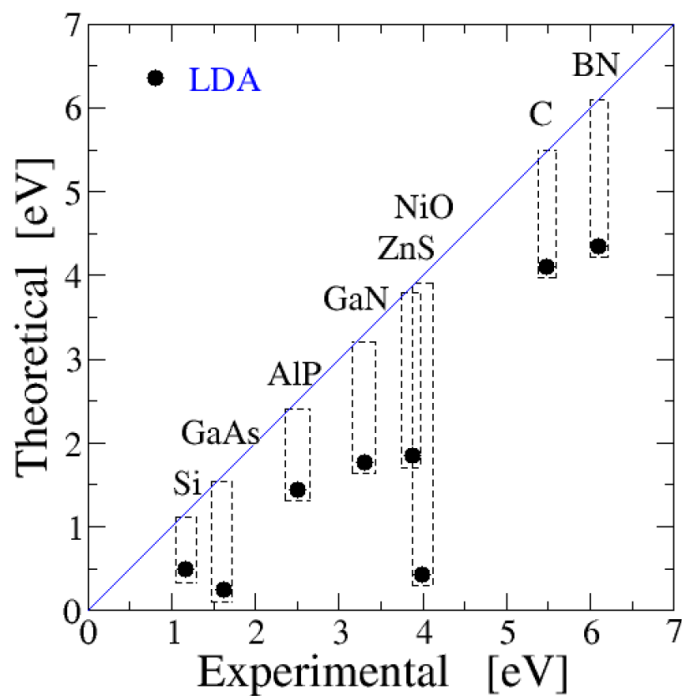
$$\varphi_{n,\mathbf{k}}(\mathbf{r}) \varphi_{n',\mathbf{k}-\mathbf{q}}^*(\mathbf{r}) = \sum_i M_{n,n'}^i(\mathbf{k}, \mathbf{q}) \chi_i^{\mathbf{q}}(\mathbf{r}). \quad (5.18)$$

BZ integration



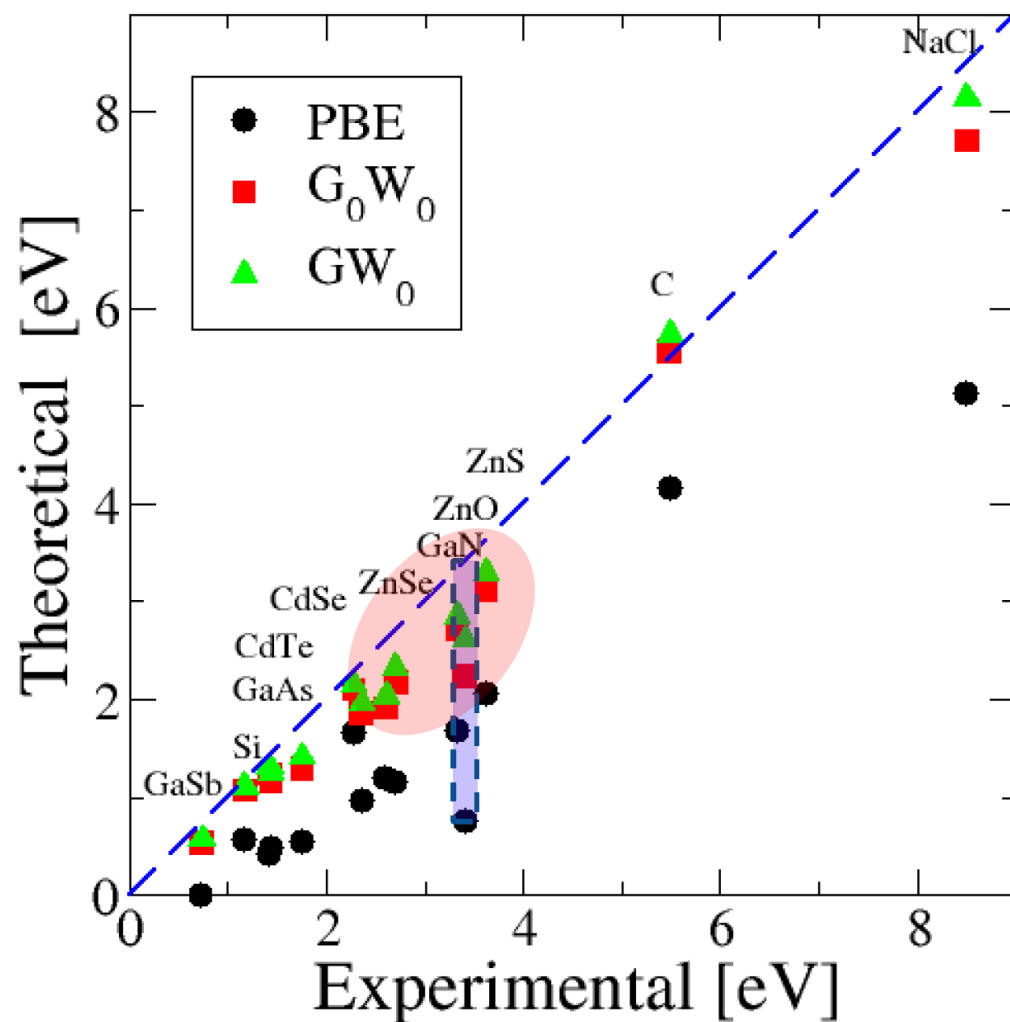


# 在实际材料中的应用



取自北京大学化学学院蒋鸿老师报告

# 在实际材料中的应用

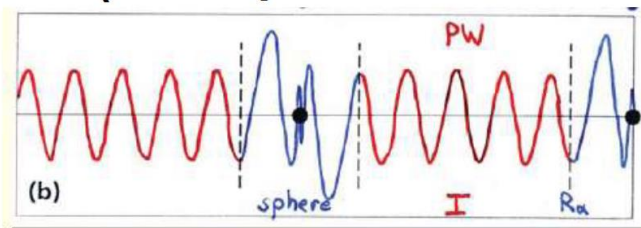


H. Jiang, *Acta Phys.-Chim. Sin.*, **26**, 1017(2010).

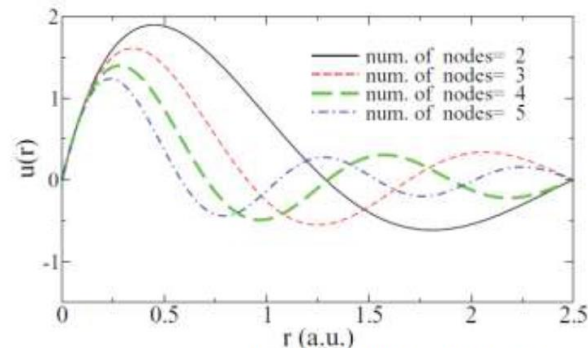
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# 在实际材料中的应用

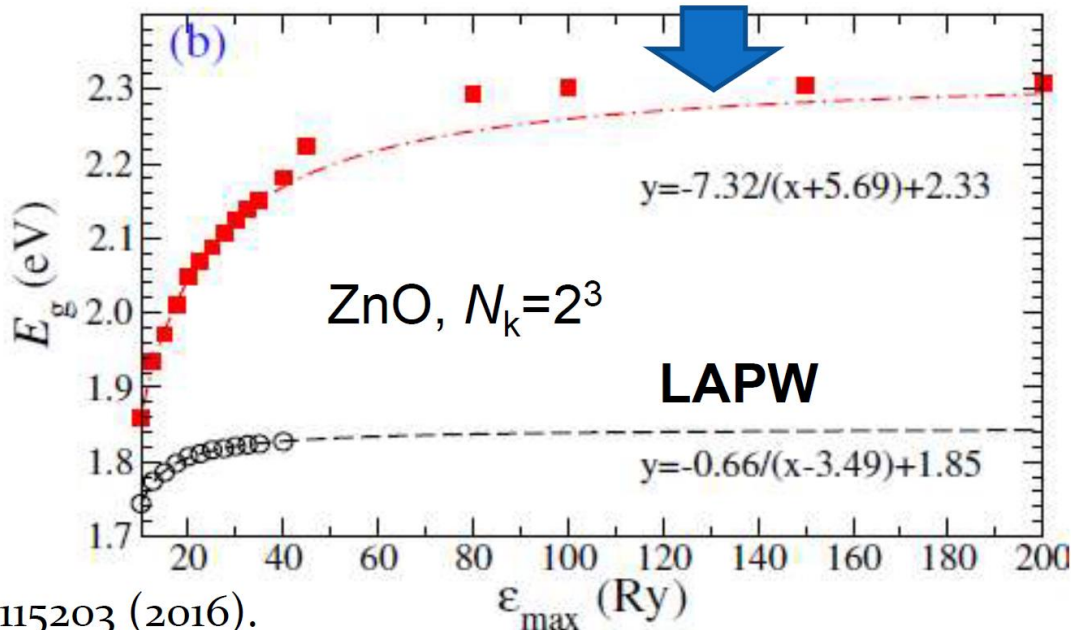
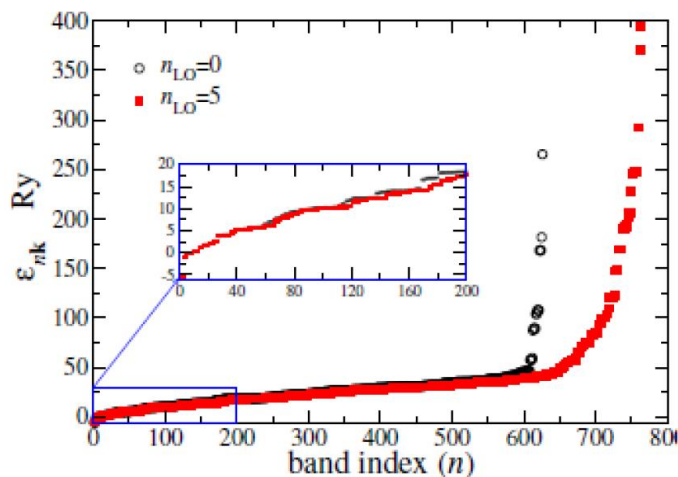
Numerically accurate GW: LAWP enhanced by high-energy local orbitals (HLOs)



+



LAPW+HLOs

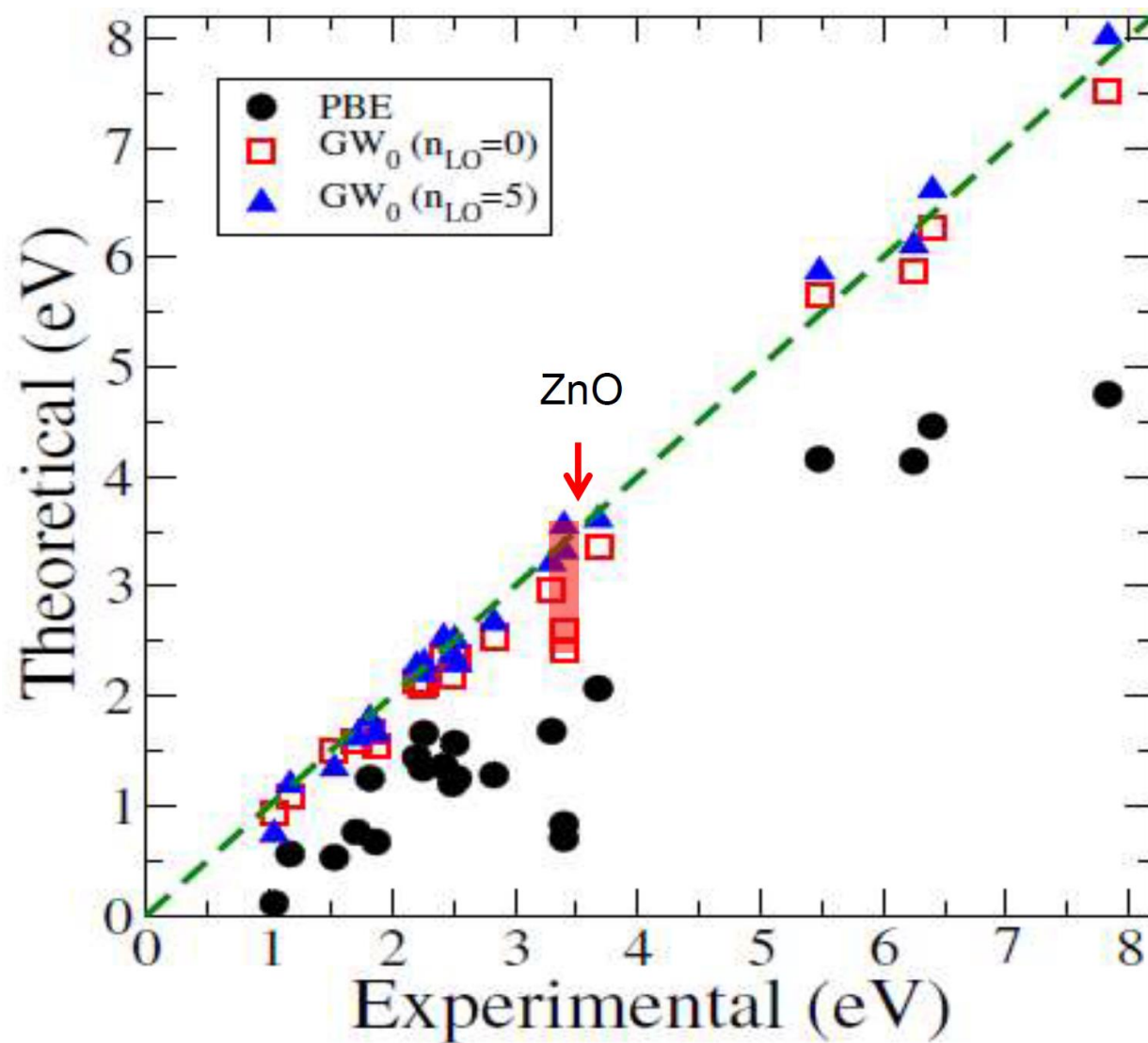


H. Jiang\*, P. Blaha, *Phys. Rev. B* **93**, 115203 (2016).

取自北京大学化学学院蒋鸿老师报告



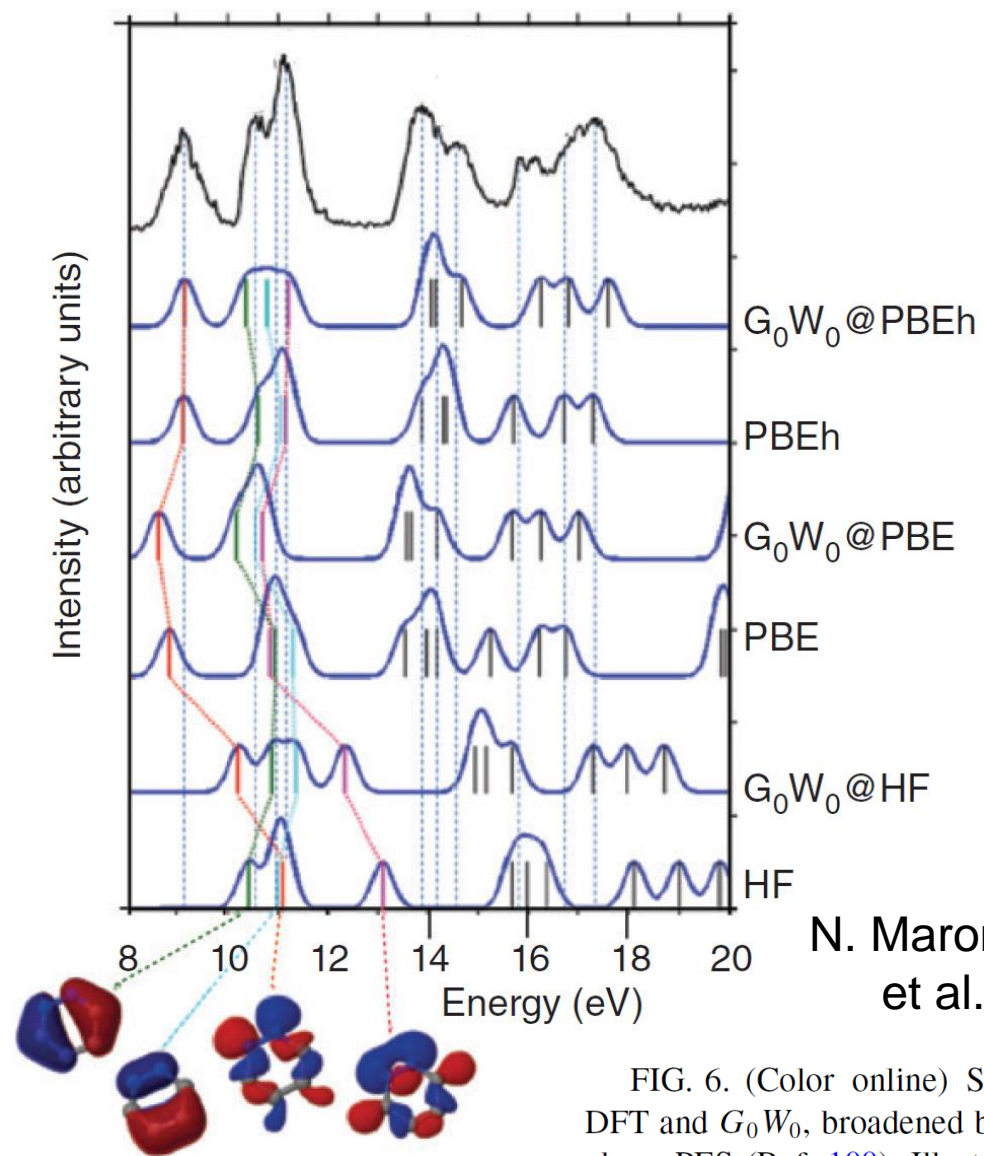
# 在实际材料中的应用



H. Jiang\*, P. Blaha, *Phys. Rev. B* **93**, 115203 (2016)

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# 在实际材料中的应用



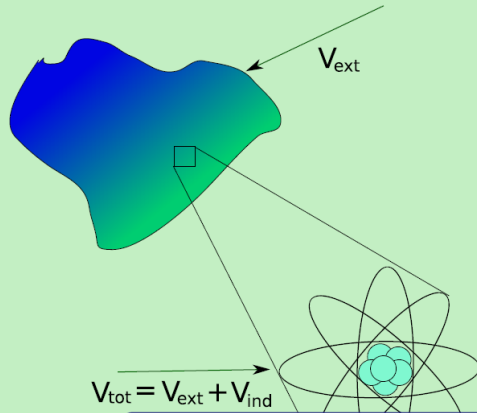
N. Marom, F. Caruso, X. G. Ren,  
et al. PRB 86, 247127 (2012)

FIG. 6. (Color online) Spectra of pyridazine, calculated with DFT and  $G_0W_0$ , broadened by a 0.3 eV Gaussian, compared to gas phase PES (Ref. 100). Illustrations of the frontier orbitals are also shown.

# Bethe-Salpeter Equation in a Nutshell

1. Dielectric Function, 一个粒子数不变时的动力学响应。

System subject to an external perturbation



$$V_{tot} = \epsilon^{-1} V_{ext}$$

$$V_{tot} = V_{ext} + V_{ind}$$

$$\mathbf{E} = \epsilon^{-1} \mathbf{D}$$

Dielectric function  $\epsilon$

EELS

R index

Abs

X-ray

$\epsilon$

$$W_0(\mathbf{r}_1, \mathbf{r}_2; \omega) = \int \epsilon^{-1}(\mathbf{r}_1, \mathbf{r}_3; \omega) v(\mathbf{r}_3, \mathbf{r}_2) d\mathbf{r}_3. \quad (5.4)$$

# Bethe-Salpeter Equation in a Nutshell

## 1. Dielectric Function, 一个粒子数不变时的动力学响应。

$$P = \frac{\delta n}{\delta v_{\text{tot}}} \quad \text{Irreducible polarizability}$$

$$\epsilon^{-1} v = v + \epsilon^{-1} v P v$$

$$\epsilon^{-1} = 1 + \epsilon^{-1} v P$$

$$\epsilon^{-1} (1 - v P) = 1$$

$$\epsilon = 1 - v P$$

$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) \quad (4.20a)$$

$$P(1, 2) = -i \int G(2, 3) G(4, 2) \Gamma(3, 4, 1) d(3, 4) \quad (4.20b)$$

$$W(1, 2) = v(1, 2) + \int W(1, 3) P(3, 4) v(4, 2) d(3, 4) \quad (4.20c)$$

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3^+) W(1, 4) \Gamma(3, 2, 4). \quad (4.20d)$$

$$\chi = \frac{\delta n}{\delta v_{\text{ext}}} \quad \text{Reducible polarizability}$$

对于外界扰动响应的RPA近似（每个粒子分别进行自己的响应，因为没有 $v_{\text{ind}}$ ，所以有关系： $\chi_0 = P_0$ 。

$$\epsilon^{-1} = \frac{\delta v_{\text{tot}}}{\delta v_{\text{ext}}} = \frac{\delta(v_{\text{ext}} + v_{\text{ind}})}{\delta v_{\text{ext}}} = 1 + \frac{\delta v_{\text{ind}}}{\delta v_{\text{ext}}} = 1 + \frac{\delta v_{\text{ind}}}{\delta n} \frac{\delta n}{\delta v_{\text{ext}}} = 1 + v \chi$$

$$1 = \epsilon \epsilon^{-1} = (1 - v P)(1 + v \chi) = 1 - v P + v \chi - v P v \chi$$

$$v \chi = v P + v P v \chi \quad \chi = P + P v \chi$$

$$\chi = P(1 + v \chi)$$

$$P = \chi(1 + v \chi)^{-1}$$

# Bethe-Salpeter Equation in a Nutshell

1. Dielectric Function, 一个粒子数不变时的动力学响应。

$$P = \frac{\delta n}{\delta v_{\text{tot}}} \quad \text{Irreducible polarizability}$$

$$\Gamma(1, 2, 3) = \delta(1, 2) \delta(2, 3) + \int d(4, 5, 6, 7) \frac{\delta \Sigma(1, 2)}{\delta G(4, 5)} G(4, 6) G(7, 5) \Gamma(6, 7, 3) \quad (4.20a)$$

$$P = -iGG\Gamma$$

$$P(1, 2) = -i \int G(2, 3) G(4, 2) \Gamma(3, 4, 1) d(3, 4) \quad (4.20b)$$

$$\Gamma = 1 + \frac{\delta \Sigma}{\delta G} GG\Gamma$$

$$W(1, 2) = v(1, 2) + \int W(1, 3) P(3, 4) v(4, 2) d(3, 4) \quad (4.20c)$$

$$GG\Gamma = GG + GG \frac{\delta \Sigma}{\delta G} GG\Gamma$$

$$\Sigma(1, 2) = i \int d(3, 4) G(1, 3^+) W(1, 4) \Gamma(3, 2, 4). \quad (4.20d)$$

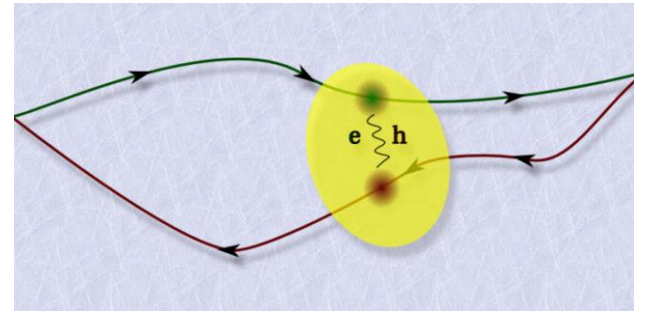
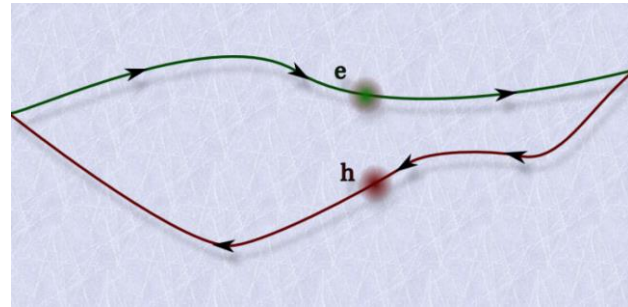
$$iP = iP_0 + iP_0 \frac{\delta \Sigma}{\delta G} GG\Gamma \quad P = P_0 + P_0 \frac{\delta \Sigma}{\delta G} GG\Gamma \quad P = P_0 + P_0 i \frac{\delta \Sigma}{\delta G} (-iGG\Gamma) \quad P = P_0 + P_0 i \frac{\delta \Sigma}{\delta G} P$$

$$\chi(1 + v\chi)^{-1} = P_0 + P_0 \frac{\delta \Sigma}{\delta G} GG\Gamma$$

$$\chi = P_0(1 + v\chi) + P_0 i \frac{\delta \Sigma}{\delta G} (-iGG\Gamma)(1 + v\chi)$$

$$\chi = P_0(1 + v\chi) + P_0 i \frac{\delta \Sigma}{\delta G} P(1 + v\chi)$$

$$\chi = P_0(1 + v\chi) + P_0 i \frac{\delta \Sigma}{\delta G} \chi = P_0 + P_0 \left( v + i \frac{\delta \Sigma}{\delta G} \right) \chi$$



# Bethe-Salpeter Equation in a Nutshell

2. 将Polarizability的起点（终点）所对应的事件分开：Bethe-Salpeter Equation。

$$\chi = \frac{\delta n}{\delta v_{\text{ext}}}$$

$$L(1, 2, 1', 2') \equiv \frac{\delta G(1, 1')}{\delta v_{\text{ext}}(2', 2)}$$

$$\chi(1, 2) = -iL(1, 2; 1^+, 2^+)$$

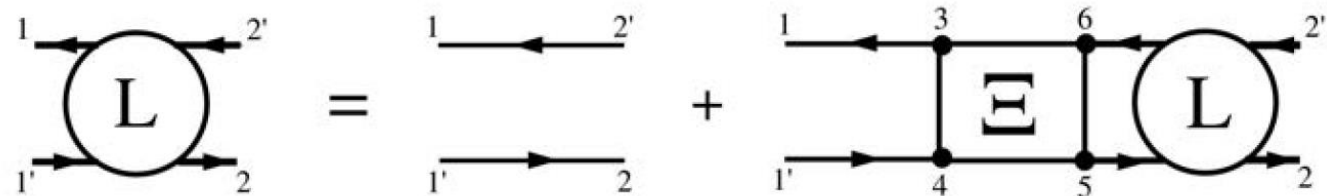
无相互作用系统： $\chi_0 = P_0$

$$\chi = P_0 + P_0 \left( v + i \frac{\delta \Sigma}{\delta G} \right) \chi$$

$$-iL = -iL_0 + (-iL_0) \left( v + i \frac{\delta \Sigma}{\delta G} \right) (-iL)$$

$$L = L_0 + (L_0) \left( v + i \frac{\delta \Sigma}{\delta G} \right) (-iL)$$

$$L = L_0 + L_0 \left( -iv + \frac{\delta \Sigma}{\delta G} \right) L$$





# Bethe-Salpeter Equation in a Nutshell

The macroscopic dielectric tensor is linked to the microscopic inverse dielectric matrix by

$$\varepsilon^M(\hat{\mathbf{q}}, \omega) = \frac{1}{\lim_{\mathbf{q} \rightarrow 0} [\varepsilon^{-1}(\mathbf{q}, \omega)]_{\mathbf{G}=0, \mathbf{G}'=0}}, \quad (5)$$

where  $\mathbf{G}$  and  $\mathbf{G}'$  are reciprocal lattice vectors. Usually, the random-phase approximation (RPA) is adopted in describing the dielectric matrix [65], using

$$\varepsilon_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega) = \delta_{\mathbf{G}, \mathbf{G}'} - \frac{4\pi e^2}{|\mathbf{G} + \mathbf{q}| |\mathbf{G}' + \mathbf{q}|} \chi_{\mathbf{G}, \mathbf{G}'}^0(\mathbf{q}, \omega). \quad (6)$$

$\chi^0(\mathbf{q}, \omega)$  is the so-called independent-particle irreducible polarizability, because under RPA the system's response to the total field (induced and incident field) resembles the case of noninteracting systems [66].

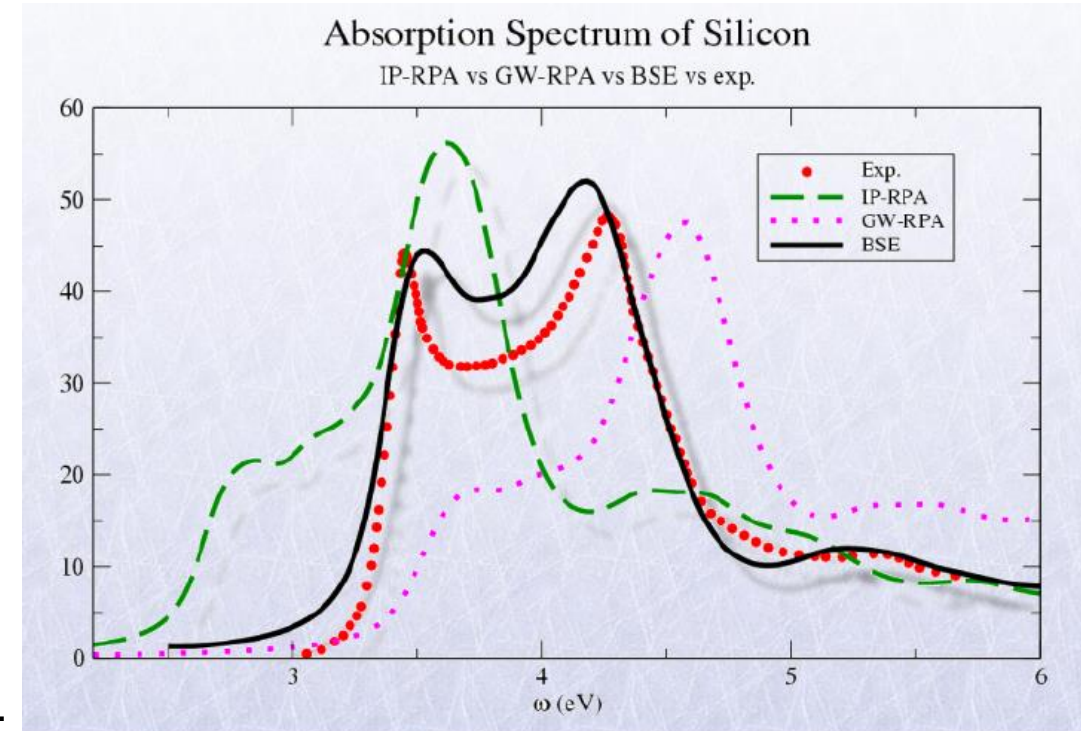
严谨度:

IPA-RPA (without local field effects) < RPA < BSE

If one neglects the local field effects [67], i.e., contributions from the off-diagonal matrix elements of  $\varepsilon_{\mathbf{G}, \mathbf{G}'}(\mathbf{q}, \omega)$  to its inverse matrix, one has

$$\varepsilon^M(\hat{\mathbf{q}}, \omega) = \lim_{\mathbf{q} \rightarrow 0} \varepsilon_{0,0}(\mathbf{q}, \omega). \quad (7)$$

This approximation is the so-called “neglecting local field effects” and also referred to as independent particle approximation (IPA). In so doing, the imaginary part of macroscopic



# Time-dependent DFT

Correlated electron motion plays a significant role in the spectra described in the previous chapters. Further, placing an atom, molecule or solid in a strong laser field reveals fascinating non-perturbative phenomena, such as non-sequential multiple-ionization (see [Chap. 18](#)), whose origins lie in the subtle ways electrons interact with each other. The direct approach to treat these problems is to solve the (non-relativistic) time-dependent Schrödinger equation for the many-electron wavefunction  $\Psi(t)$ :

$$\hat{H}(t)\Psi(t) = i\frac{\partial\Psi(t)}{\partial t}, \quad \hat{H}(t) = \hat{T} + \hat{V}_{\text{ee}} + \hat{V}_{\text{ext}}(t) \quad (4.1)$$

for a given initial wavefunction  $\Psi(0)$ . Here, the kinetic energy and electron–electron repulsion, are, respectively:

$$\hat{T} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2, \quad \text{and} \quad \hat{V}_{\text{ee}} = \frac{1}{2} \sum_{i \neq j}^N \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|}, \quad (4.2)$$

and the “external potential” represents the potential the electrons experience due to the nuclear attraction and due to any field applied to the system (e.g. laser):

$$\hat{V}_{\text{ext}}(t) = \sum_{i=1}^N v_{\text{ext}}(\mathbf{r}_i, t). \quad (4.3)$$



# Time-dependent DFT

For example,  $v_{\text{ext}}(\mathbf{r}_i, t)$  can represent the Coulomb interaction of the electrons with a set of nuclei, possibly moving along some classical path,

$$v_{\text{ext}}(\mathbf{r}, t) = - \sum_{\nu=1}^{N_n} \frac{Z_{\nu}}{|\mathbf{r} - \mathbf{R}_{\nu}(t)|}, \quad (4.4)$$

where  $Z_{\nu}$  and  $\mathbf{R}_{\nu}$  denote the charge and position of the nucleus  $\nu$ , and  $N_n$  stands for the total number of nuclei in the system. This may be useful to study, e.g., scattering experiments, chemical reactions, etc. Another example is the interaction with external fields, e.g. for a system illuminated by a laser beam we can write, in the dipole approximation,

$$v_{\text{ext}}(\mathbf{r}, t) = E f(t) \sin(\omega t) \mathbf{r} \cdot \boldsymbol{\alpha} - \sum_{\nu=1}^{N_n} \frac{Z_{\nu}}{|\mathbf{r} - \mathbf{R}_{\nu}|} \quad (4.5)$$

where  $\boldsymbol{\alpha}$ ,  $\omega$  and  $E$  are the polarization, the frequency and the amplitude of the laser, respectively. The function  $f(t)$  is an envelope that describes the temporal shape of the laser pulse. We use atomic units ( $e^2 = \hbar = m = 1$ ) throughout this chapter; all distances are in Bohr, energies in Hartrees (1 H = 27.21 eV = 627.5 kcal/mol), and times in units of  $2.419 \times 10^{-17}$  s.

Solving Eq. 4.1 is an exceedingly difficult task.

# Time-dependent DFT

function of the oxygen atom, even on a coarse grid. Physically, we are instead interested in integrated quantities, such as one- or two-body probability-densities, which, traditionally can be extracted from this foreboding  $\Psi$ . However, a method that could yield such quantities directly, by-passing the need to calculate  $\Psi$ , would be highly attractive. This is the idea of density-functional theories. In fact, in 1964, Hohenberg and Kohn (1964), proved that *all* observable properties of a static many-electron system can be extracted exactly, in principle, from the one-body ground-state density alone. Twenty years later, Runge and Gross extended this to time-dependent systems, showing that all observable properties of a many-electron system, beginning in a given initial state  $\Psi(0)$ , may be extracted from the one-body time-dependent density alone (Runge and Gross 1984). What has made (TD)DFT so incredibly successful is the Kohn–Sham (KS) system: the density of the interacting many-electron system is obtained as the density of an auxiliary system of non-interacting fermions, living in a one-body potential. The exponential scaling with system-size that the solution to Eq. 4.1 requires is replaced in TDDFT by the much gentler  $N^3$  or  $N^2$  scaling (depending on the implementation) (Marques 2006), opening the door to the quantum mechanical study of much larger systems, from nanoscale devices to biomolecules. (See Chaps. 19–21 for details on the numerical issues). Although the ground-state and time-dependent theories have a similar flavor, and *modus operandi*, their proofs and functionals are quite distinct.

# Time-dependent DFT

## 4.2 One-to-One Density-Potential Mapping

The central theorem of TDDFT (the Runge–Gross theorem) proves that there is a one-to-one correspondence between the external (time-dependent) potential,  $v_{\text{ext}}(\mathbf{r}, t)$ , and the electronic one-body density,  $n(\mathbf{r}, t)$ , for many-body systems evolving from a fixed initial state  $\Psi_0$  (Runge and Gross 1984). The density  $n(\mathbf{r}, t)$  is the probability (normalized to the particle number  $N$ ) of finding any one electron, of any spin  $\sigma$ , at position  $\mathbf{r}$ :

$$n(\mathbf{r}, t) = N \sum_{\sigma, \sigma_2 \dots \sigma_N} \int d^3\mathbf{r}_2 \cdots \int d^3\mathbf{r}_N |\Psi(\mathbf{r}\sigma, \mathbf{r}_2\sigma_2 \cdots \mathbf{r}_N\sigma_N, t)|^2 \quad (4.6)$$

The implications of this theorem are enormous: if we know only the time-dependent density of a system, evolving from a given initial state, then this identifies the external potential that produced this density. The external potential completely identifies the Hamiltonian (the other terms given by Eq. 4.2 are determined from the fact that we are dealing with electrons, with  $N$  being the integral of the density of Eq. 4.6 over  $\mathbf{r}$ .) The time-dependent Schrödinger equation can then be solved, in principle, and all properties of the system obtained. That is, for this given initial-state, the electronic density, a function of just three spatial variables and time, determines all other properties of the interacting many-electron system.

# Time-dependent DFT

This remarkable statement is the analogue of the Hohenberg-Kohn theorem for ground-state DFT, where the situation is somewhat simpler: the density-potential map there holds only for the ground-state, so there is no time-dependence and no dependence on the initial state. The Hohenberg-Kohn proof is based on the Rayleigh-Ritz minimum principle for the energy. A straightforward extension to the time-dependent domain is not possible since a minimum principle is not available in this case.

Instead, the proof for a 1–1 mapping between time-dependent potentials and time-dependent densities is based on considering the quantum-mechanical equation of motion for the current-density, for a Hamiltonian of the form of Eqs. 4.1–4.3. The proof requires the potentials  $v_{\text{ext}}(\mathbf{r}, t)$  to be time-analytic around the initial time, i.e. that they equal their Taylor-series expansions in  $t$  around  $t = 0$ , for a finite time interval:

$$v_{\text{ext}}(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v_{\text{ext},k}(\mathbf{r}) t^k. \quad (4.7)$$

The aim is to show that two densities  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  evolving from a common initial state  $\Psi_0$  under the influence of the potentials  $v_{\text{ext}}(\mathbf{r}, t)$  and  $v'_{\text{ext}}(\mathbf{r}, t)$  are always different provided that the potentials differ by more than a purely time-dependent function:

$$v_{\text{ext}}(\mathbf{r}, t) \neq v'_{\text{ext}}(\mathbf{r}, t) + c(t). \quad (4.8)$$

# Time-dependent DFT

The above condition is a physical one, representing simply a gauge-freedom. A purely time-dependent constant in the potential cannot alter the physics: if two potentials differ only by a purely time-dependent function, their resulting wavefunctions differ only by a purely time-dependent phase factor. Their resulting densities are identical. All variables that correspond to expectation values of Hermitian operators are unaffected by such a purely time-dependent phase. There is an analogous condition in the ground-state proof of Hohenberg and Kohn. Equation 4.8 is equivalent to the statement that for the expansion coefficients  $v_{\text{ext},k}(\mathbf{r})$  and  $v'_{\text{ext},k}(\mathbf{r})$  [where, as in Eq. 4.7,  $v'_{\text{ext}}(\mathbf{r}, t) = \sum_{k=0}^{\infty} \frac{1}{k!} v'_{\text{ext},k}(\mathbf{r}) t^k$  ] there exists a smallest integer  $k \geq 0$  such that

$$v_{\text{ext},k}(\mathbf{r}) - v'_{\text{ext},k}(\mathbf{r}) = \left. \frac{\partial^k}{\partial t^k} [v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t)] \right|_{t=0} \neq \text{const.} \quad (4.9)$$

The initial state  $\Psi_0$  need not be the ground-state or any stationary state of the initial potential, which means that “sudden switching” is covered by the RG theorem. But

# Time-dependent DFT

The first step of the proof demonstrates that the current-densities

$$\mathbf{j}(\mathbf{r}, t) = \langle \Psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle \quad (4.10)$$

and

$$\mathbf{j}'(\mathbf{r}, t) = \langle \Psi'(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi'(t) \rangle \quad (4.11)$$

are different for different potentials  $v_{\text{ext}}$  and  $v'_{\text{ext}}$ . Here,

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{2i} \sum_{i=1}^N [\nabla_i \delta(\mathbf{r} - \mathbf{r}_i) + \delta(\mathbf{r} - \mathbf{r}_i) \nabla_i] \quad (4.12)$$

is the usual paramagnetic current-density operator. In the second step, use of the continuity equation shows that the densities  $n$  and  $n'$  are different. We now proceed with the details.



# Time-dependent DFT

*Step 1* We apply the equation of motion for the expectation value of a general operator  $\hat{Q}(t)$ ,

$$\frac{\partial}{\partial t} \langle \Psi(t) | \hat{Q}(t) | \Psi(t) \rangle = \langle \Psi(t) | \left( \frac{\partial \hat{Q}}{\partial t} - i[\hat{Q}(t), \hat{H}(t)] \right) | \Psi(t) \rangle, \quad (4.13)$$

to the current densities:

$$\frac{\partial}{\partial t} \mathbf{j}(\mathbf{r}, t) = \frac{\partial}{\partial t} \langle \Psi(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi(t) \rangle = -i \langle \Psi(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)] | \Psi(t) \rangle \quad (4.14a)$$

$$\frac{\partial}{\partial t} \mathbf{j}'(\mathbf{r}, t) = \frac{\partial}{\partial t} \langle \Psi'(t) | \hat{\mathbf{j}}(\mathbf{r}) | \Psi'(t) \rangle = -i \langle \Psi'(t) | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}'(t)] | \Psi'(t) \rangle, \quad (4.14b)$$

and take their difference evaluated at the initial time. Since  $\Psi$  and  $\Psi'$  evolve from the same initial state

$$\Psi(t=0) = \Psi'(t=0) = \Psi_0, \quad (4.15)$$

# Time-dependent DFT

and the corresponding Hamiltonians differ only in their external potentials, we have

$$\begin{aligned} \left. \frac{\partial}{\partial t} [\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)] \right|_{t=0} &= -i \langle \Psi_0 | [\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(0) - \hat{H}'(0)] | \Psi_0 \rangle \\ &= -n_0(\mathbf{r}) \nabla [v_{\text{ext}}(\mathbf{r}, 0) - v'_{\text{ext}}(\mathbf{r}, 0)] \end{aligned} \quad (4.16)$$

where  $n_0(\mathbf{r})$  is the initial density. Now, if the condition (4.9) is satisfied for  $k = 0$  the right-hand side of (4.16) cannot vanish identically and  $\mathbf{j}$  and  $\mathbf{j}'$  will become different infinitesimally later than  $t = 0$ . If the smallest integer  $k$  for which Eq. 4.9 holds is greater than zero, we use Eq. 4.13 ( $k + 1$ ) times. That is, as for  $k = 0$  above where we used  $\hat{Q}(t) = \hat{\mathbf{j}}(\mathbf{r})$  in Eq. 4.13, for  $k = 1$ , we take  $\hat{Q}(t) = -i[\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)]$ ; for general  $k$ ,  $\hat{Q}(t) = (-i)^k [[[\hat{\mathbf{j}}(\mathbf{r}), \hat{H}(t)], \hat{H}(t)] \dots \hat{H}(t)]_k$  meaning there are  $k$  nested commutators to take. After some algebra<sup>1</sup>:

$$\left( \frac{\partial}{\partial t} \right)^{k+1} [\mathbf{j}(\mathbf{r}, t) - \mathbf{j}'(\mathbf{r}, t)] \Big|_{t=0} = -n_0(\mathbf{r}) \nabla w_k(\mathbf{r}) \neq 0 \quad (4.17)$$

with

$$w_k(\mathbf{r}) = \left( \frac{\partial}{\partial t} \right)^k [v_{\text{ext}}(\mathbf{r}, t) - v'_{\text{ext}}(\mathbf{r}, t)] \Big|_{t=0}. \quad (4.18)$$



# Time-dependent DFT

Once again, we conclude that infinitesimally later than the initial time,

$$\mathbf{j}(\mathbf{r}, t) \neq \mathbf{j}'(\mathbf{r}, t). \quad (4.19)$$

This first step thus proves that the current-densities evolving from the same initial state in two physically distinct potentials, will differ. That is, it proves a one-to-one correspondence between current-densities and potentials, for a given initial-state.

# Time-dependent DFT

*Step 2* To prove the corresponding statement for the densities we use the continuity equation

$$\frac{\partial n(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j}(\mathbf{r}, t) \quad (4.20)$$

to calculate the  $(k + 2)$ nd time-derivative of the density  $n(\mathbf{r}, t)$  and likewise of the density  $n'(\mathbf{r}, t)$ . Taking the difference of the two at the initial time  $t = 0$  and inserting Eq. 4.18 yields

$$\left( \frac{\partial}{\partial t} \right)^{k+2} [n(\mathbf{r}, t) - n'(\mathbf{r}, t)] \Big|_{t=0} = \nabla \cdot [n_0(\mathbf{r}) \nabla w_k(\mathbf{r})]. \quad (4.21)$$

Now, if there was no divergence-operator on the r.h.s., our task would be complete, showing that the densities  $n(\mathbf{r}, t)$  and  $n'(\mathbf{r}, t)$  will become different infinitesimally later than  $t = 0$ . To show that the divergence does not render the r.h.s. zero, thus allowing an escape from this conclusion, we consider the integral

$$\begin{aligned} \int d^3r n_0(\mathbf{r}) [\nabla w_k(\mathbf{r})]^2 &= - \int d^3r w_k(\mathbf{r}) \nabla \cdot [n_0(\mathbf{r}) \nabla w_k(\mathbf{r})] \\ &\quad + \oint d\mathbf{S} \cdot [n_0(\mathbf{r}) w_k(\mathbf{r}) \nabla w_k(\mathbf{r})], \end{aligned} \quad (4.22)$$

where we have used Green's theorem. For physically reasonable potentials (i.e. potentials arising from normalizable external charge densities), the surface integral on the right vanishes (Gross and Kohn 1990) (more details are given in Sect. 4.4.1). Since the integrand on the left-hand side is strictly positive or zero, the first term on the right must be strictly positive. That is,  $\nabla \cdot [n_0(\mathbf{r}) \nabla w_k(\mathbf{r})]$  cannot be zero everywhere. This completes the proof of the theorem.

We have shown that densities evolving from the same initial wavefunction  $\Psi_0$  in different potentials must be different. Schematically, the Runge-Gross theorem shows

$$\Psi_0 : v_{\text{ext}} \xleftrightarrow{1-1} n. \quad (4.23)$$

The backward arrow, that a given time-dependent density points to a single time-dependent potential for a given initial state, has been proven above. The forward arrow follows directly from the uniqueness of solutions to the time-dependent Schrödinger equation.

Due to the one-to-one correspondence, for a given initial state, the time-dependent density determines the potential up to a purely time-dependent constant. The wavefunction is therefore determined up to a purely-time-dependent phase, as discussed at the beginning of this section, and so can be regarded as a functional of the density and initial state:

$$\Psi(t) = e^{-i\alpha(t)} \Psi[n, \Psi_0](t). \quad (4.24)$$

# Time-dependent DFT

As a consequence, the expectation value of any quantum mechanical Hermitian operator  $\hat{Q}(t)$  is a *unique* functional of the density and initial state (and, not surprisingly, the ambiguity in the phase cancels out):

$$Q[n, \Psi_0](t) = \langle \Psi[n, \Psi_0](t) | \hat{Q}(t) | \Psi[n, \Psi_0](t) \rangle. \quad (4.25)$$

We also note that the particular form of the Coulomb interaction did not enter into the proof. In fact, the proof applies not just to electrons, but to *any* system of identical particles, interacting with any (but fixed) particle-interaction, and obeying either fermionic or bosonic statistics.

# Time-dependent DFT

## 4.3 Time-Dependent Kohn–Sham Equations

Finding functionals directly in terms of the density can be rather difficult. In particular, it is not known how to write the kinetic energy as an explicit functional of the density. The same problem occurs in ground-state DFT, where the search for accurate kinetic-energy density-functionals is an active research area. Instead, like in the ground-state theory, we turn to a non-interacting system of fermions called the Kohn–Sham (KS) system, defined such that it exactly reproduces the density of the true interacting system. A large part of the kinetic energy of the true system is obtained directly as an orbital-functional, evaluating the usual kinetic energy operator on the KS orbitals. (The rest, along with other many-electron effects, is contained in the exchange-correlation potential.) All properties of the true system can be extracted from the density of the KS system.

$$v_{\text{ext}}[n, \Psi_0](\mathbf{r}, t) \xleftrightarrow{1-1} n(\mathbf{r}, t) \xleftrightarrow{1-1} v_{\text{KS}}[n, \Phi_0](\mathbf{r}, t).$$

$$n(\mathbf{r}, t) = \sum_{j=1}^N |\varphi_j(\mathbf{r}, t)|^2 \quad (4.26)$$

with orbitals  $\varphi_j(\mathbf{r}, t)$  satisfying the time-dependent KS equation

$$i\frac{\partial}{\partial t}\varphi_j(\mathbf{r}, t) = \left[ -\frac{\nabla^2}{2} + v_{\text{KS}}[n; \Phi_0](\mathbf{r}, t) \right] \varphi_j(\mathbf{r}, t). \quad (4.27)$$

Analogously to the ground-state case,  $v_{\text{KS}}$  is decomposed into three terms:

$$v_{\text{KS}}[n; \Phi_0](\mathbf{r}, t) = v_{\text{ext}}[n; \Psi_0](\mathbf{r}, t) + \int d^3r' \frac{n(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|} + v_{\text{xc}}[n; \Psi_0, \Phi_0](\mathbf{r}, t), \quad (4.28)$$

# Time-dependent DFT

where  $v_{\text{ext}}[n; \Psi_0](\mathbf{r}, t)$  is the external time-dependent field. The second term on the right-hand side of Eq. 4.28 is the time-dependent Hartree potential, describing the interaction of classical electronic charge distributions, while the third term is the exchange-correlation (xc) potential which, in practice, has to be approximated. Equation 4.28 defines the xc potential: it, added to the classical Hartree potential, is the difference between the external potential that generates density  $n(\mathbf{r}, t)$  in an interacting system starting in initial state  $\Psi_0$  and the one-body potential that generates this same density in a non-interacting system starting in initial state  $\Phi_0$ .

