29 The Exchange-Correlation Potential in the Adiabatic-Connection Fluctuation-Dissipation Framework

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29.1 Introduction

As shown in the previous chapter, time-dependent DFT – which is basically an excited-state theory – also provides useful insight into the ground-state properties. Indeed, non-local approximations for the correlation energy $E_c[n]$ can be built upon TDDFT using the adiabatic connection and fluctuation dissipation (ACFD) theorems [Langreth 1975, Langreth 1977]. The random-phase approximation (RPA) is the prototype of these ACFD functionals. It has been applied to the homogeneous electron gas more than three decades ago [Nozières 1958, von Barth 1972, Vosko 1980], then to jellium slabs and surfaces [Pitarke 1998, Pitarke 2001, Dobson 1999, Kurth 1999]; the calculation of the ground-state energy surface of simple diatomic molecules [Furche 2001c, Fuchs 2002, Aryasetiawan 2002, Fuchs 2003, Fuchs 2005b] (H_2, N_2 . . .) and solids [Miyake 2002, Marini 2006] (Si, Na, NaCl, h-BN . . .) has been achieved much more recently. Though demanding, the RPA improves over the LDA and GGA in many respects: for example, the RPA accounts for long-range effects such as van der Waals interactions [Dobson 1996, Kohn 1998, Lein 1999] and properly dissociates molecules with electron pair bonds such as H_2 [Fuchs 2005b]. The RPA however misses important short-range correlations [Singwi 1968], the total energy being usually too low [Fuchs 2002] (though isoelectronic total energy differences are believed to be quite accurate [Yan 2000]). This deficiency can however be cured with LDA-like corrections [Kurth 1999, Yan 2000] or using refined time-dependent DFT kernels [Fuchs 2002, Lein 2000b]. As a matter of fact, the RPA is just a particular realization of a large class of functionals, leaving plenty of opportunities for improvement.

The correlation potential $v_c(\boldsymbol{r})$ that is derived from a given approximation for $E_c[n]$ is a key ingredient of density functional theory. ACFD potentials would open the way for self-consistent calculations and could provide valuable information about the underlying functionals. In this chapter, we derive the expression for the RPA exchange-correlation potential $v_{xc}^{RPA}(\boldsymbol{r})$. We show that $v_{xc}^{RPA}(\boldsymbol{r})$ satisfies the so-called linear-response Sham-Schlüter equation [Sham 1983, Sham 1985, Casida 1995b]. We also provide an approximate solution of this equation, that is much simpler to compute while being likely of reasonable accuracy. We then discuss the asymptotic behavior of $v_{xc}^{RPA}(\boldsymbol{r})$

in finite systems such as atoms [Niquet 2003a, Niquet 2003b, Niquet 2003c, Niquet 2005], which reveals much physics as well as the merits and deficiencies of the RPA. A more extensive discussion of the ACFD potentials (including the PGG and ALDA kernels) can be found in [Niquet 2003c].

Another v_{xc}-related issue is the well-known "bandgap problem". Indeed, the Kohn-Sham (KS) bandgap energy $\varepsilon_{\mathrm{g}} = \varepsilon_{\mathrm{c}} - \varepsilon_{\mathrm{v}}$ is usually found much lower than the experimental bandgap (ε_{v} and ε_{c} being respectively the highest occupied and lowest unoccupied KS energies). As a matter of fact, ε_{g} might differ from the interacting bandgap energy $E_{\mathrm{g}} = E(N+1) + E(N-1) - 2E(N)$, where $E(N)$ is the total energy of the $N-$electron system, due to the existence of a derivative discontinuity in the exchange-correlation functional [Sham 1983, Perdew 1982, Perdew 1983, Sham 1985b]. In practice, the fundamental bandgap energy and quasiparticle band structure of a solid are thus computed with many-body Green function techniques such as the GW method [Hedin 1969, Mattuck 1967]. In principle, the Green function G should be updated through Dyson equation until many-body self-consistency is achieved [Baym 1961, Baym 1962]. In most cases, however, the GW self-energy is calculated using KS orbitals and energies as input, thus leaving out self-consistency. This "$G_{\mathrm{KS}}W_{\mathrm{KS}}$" (also known as "$G_0 W_0$") approach has been successfully applied to a wide variety of materials [Hybertsen 1985, Hybertsen 1986, Godby 1988, Aulbur 2000]. There has been, however, recent controversy about the effects of many-body self-consistency on the quasiparticle band structure and about the rationale behind the $G_{\mathrm{KS}}W_{\mathrm{KS}}$ approach [Schöne 1998, Ku 2002]. In this chapter, we show how the RPA functional provides such a rationale within a consistent DFT framework [Niquet 2004].

The chapter is organized as follows: the expression of the RPA potential is first derived in Sect. 29.2; its asymptotic properties are then discussed in Sect. 29.3; the RPA bandgap problem is investigated in Sect. 29.4.

29.2 The RPA Exchange-Correlation Potential

In this section, we show that $v_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$ satisfies the so-called linear-response Sham-Schlüter equation [Sham 1983, Sham 1985, Casida 1995b]. We also discuss an approximate (but reasonably accurate) solution of this equation. For the sake of simplicity, we restrict ourselves to spin-compensated N-electron systems.

We first focus on the RPA correlation potential $v_{\mathrm{c}}^{\mathrm{RPA}}(\boldsymbol{r}) = \delta E_{\mathrm{c}}^{\mathrm{RPA}}/\delta n(\boldsymbol{r})$. The RPA correlation energy reads, after integration over the coupling constant[1] [Niquet 2003c]:

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[1] Please note that RPA-like approximations can also be derived from many-body perturbation theory starting from variational functionals of the Green function [Almbladh 1999]. Different flavours of these functionals (Luttinger-Ward

$$E_c^{\text{RPA}}[n] = \frac{1}{2} \int \frac{\mathrm{d}u}{2\pi} \operatorname{Tr} \{\ln[1 - v_{\text{ee}}\chi_{\text{KS}}(iu)] + v_{\text{ee}}\chi_{\text{KS}}(iu)\} \, . \tag{29.1}$$

At variance with the LDA or GGA, (29.1) is an *explicit* functional the KS orbitals and energies, hence an *implicit* functional of the density. The derivation of $v_c^{\text{RPA}}(\boldsymbol{r})$ is thus somewhat involved. Using the relation:

$$\frac{\delta \operatorname{Tr}\{\ln A(iu)\}}{\delta n(\boldsymbol{r})} = \operatorname{Tr}\left\{ A^{-1}(iu)\frac{\delta A(iu)}{\delta n(\boldsymbol{r})} \right\} \tag{29.2}$$

we indeed get at once:

$$v_c^{\text{RPA}}(\boldsymbol{r}) = -\frac{1}{2} \int \frac{\mathrm{d}u}{2\pi} \operatorname{Tr}\left\{ [W_{\text{KS}}(iu) - v_{\text{ee}}]\frac{\delta\chi_{\text{KS}}(iu)}{\delta n(\boldsymbol{r})} \right\} \, , \tag{29.3}$$

where $W_{\text{KS}}(iu) = [1 - v_{\text{ee}}\chi_{\text{KS}}(iu)]^{-1}v_{\text{ee}}$ is the RPA screened Coulomb interaction. We are now left with $\delta\chi_{\text{KS}}(iu)/\delta n(\boldsymbol{r})$. We proceed taking advantage of the much simpler dependence of $\chi_{\text{KS}}(iu)$ on the KS Green function $G_{\text{KS}}(iu)$. Indeed (as can be verified by straightforward integration),

$$\chi_{\text{KS}}(\boldsymbol{r}, \boldsymbol{r}', iu) = 2 \int \frac{\mathrm{d}v}{2\pi} G_{\text{KS}}(\boldsymbol{r}, \boldsymbol{r}', iu + iv)G_{\text{KS}}(\boldsymbol{r}', \boldsymbol{r}, iv) \, , \tag{29.4}$$

where:

$$G_{\text{KS}}(\boldsymbol{r}, \boldsymbol{r}', iu) = \frac{1}{iu - \hat{H}_{\text{KS}}} = \sum_j \frac{\varphi_j(\boldsymbol{r})\varphi_j^*(\boldsymbol{r}')}{iu - \varepsilon_j} \, . \tag{29.5}$$

Here $\hat{H}_{\text{KS}} = \hat{T} + v_{\text{KS}}$ is the KS Hamiltonian, $\hat{T}$ being the kinetic energy operator and v_{KS} the Kohn-Sham potential. The derivative chain rule then yields:

$$\frac{\delta\chi_{\text{KS}}(\boldsymbol{r}, \boldsymbol{r}', iu)}{\delta n(\boldsymbol{r})} = \int \mathrm{d}w \int \mathrm{d}^3 r_1 \int \mathrm{d}^3 r_2 \int \mathrm{d}^3 r_3$$
$$\frac{\delta\chi_{\text{KS}}(\boldsymbol{r}, \boldsymbol{r}', iu)}{\delta G_{\text{KS}}(\boldsymbol{r}_1, \boldsymbol{r}_2, iw)} \frac{\delta G_{\text{KS}}(\boldsymbol{r}_1, \boldsymbol{r}_2, iw)}{\delta v_{\text{KS}}(\boldsymbol{r}_3)} \frac{\delta v_{\text{KS}}(\boldsymbol{r}_3)}{\delta n(\boldsymbol{r})} \, . \tag{29.6}$$

The last derivative on the right-hand side, $\delta v_{\text{KS}}(\boldsymbol{r}_3)/\delta n(\boldsymbol{r})$, is just the inverse of the static KS density-density response function, $\chi_{\text{KS}}^{-1}(\boldsymbol{r}_3, \boldsymbol{r}, iu = 0)$ [since by definition $\chi_{\text{KS}}(\boldsymbol{r}, \boldsymbol{r}_3, iu = 0) = \delta n(\boldsymbol{r})/\delta v_{\text{KS}}(\boldsymbol{r}_3)$]. As for the second derivative, we have (in a compact, matrix-like notation):

$$\frac{\delta[G_{\text{KS}}(iw)G_{\text{KS}}^{-1}(iw)]}{\delta v_{\text{KS}}(\boldsymbol{r}_3)} = 0 \Rightarrow \frac{\delta G_{\text{KS}}(iw)}{\delta v_{\text{KS}}(\boldsymbol{r}_3)} = -G_{\text{KS}}(iw)\frac{\delta G_{\text{KS}}^{-1}(iw)}{\delta v_{\text{KS}}(\boldsymbol{r}_3)}G_{\text{KS}}(iw) \, . \tag{29.7}$$

[Luttinger 1960], Nozières [Nozières 1964]...) however yield different approximations for the correlation energy, and thus different potentials. The original RPA as given by (29.1) can actually be derived from Nozières' functional [Nozières 1964].

Moreover, the functional derivative of the inverse KS Green function $G_{KS}^{-1}(iw) = iw - \hat{T} - v_{KS}$ is just:

$$\frac{\delta G_{KS}^{-1}(\boldsymbol{r}_4, \boldsymbol{r}_5, iw)}{\delta v_{KS}(\boldsymbol{r}_3)} = -\delta(\boldsymbol{r}_3 - \boldsymbol{r}_4)\delta(\boldsymbol{r}_3 - \boldsymbol{r}_5). \tag{29.8}$$

Last, the derivative of $\chi_{KS}(iu)$ with respect to $G_{KS}(iw)$ directly follows from (29.4):

$$\frac{\delta \chi_{KS}(\boldsymbol{r}, \boldsymbol{r}', iu)}{\delta G_{KS}(\boldsymbol{r}_1, \boldsymbol{r}_2, iw)} = \frac{2}{2\pi}\delta(\boldsymbol{r} - \boldsymbol{r}_1)\delta(\boldsymbol{r}' - \boldsymbol{r}_2)G_{KS}(\boldsymbol{r}_2, \boldsymbol{r}_1, iw - iu)$$

$$+ \frac{2}{2\pi}\delta(\boldsymbol{r}' - \boldsymbol{r}_1)\delta(\boldsymbol{r} - \boldsymbol{r}_2)G_{KS}(\boldsymbol{r}_2, \boldsymbol{r}_1, iw + iu). \tag{29.9}$$

Backward substitution of (29.9), (29.8), (29.7) and (29.6) into (29.3) finally yields the following expression for the RPA correlation potential:

$$v_c^{RPA}(\boldsymbol{r}) = \int d^3r' \, \chi_{KS}^{-1}(\boldsymbol{r}, \boldsymbol{r}', iu = 0)\rho_c(\boldsymbol{r}'), \tag{29.10}$$

where:

$$\rho_c(\boldsymbol{r}) = 2\int \frac{du}{2\pi}\int d^3r_1 \int d^3r_2 \, G_{KS}(\boldsymbol{r}, \boldsymbol{r}_1, iu)\Sigma_c(\boldsymbol{r}_1, \boldsymbol{r}_2, iu)G_{KS}(\boldsymbol{r}_2, \boldsymbol{r}, iu). \tag{29.11}$$

and $\Sigma_c(\boldsymbol{r}_1, \boldsymbol{r}_2, iu)$ is the correlation part of the so-called imaginary-frequency $G_{KS}W_{KS}$ self-energy [Hedin 1969] (also see Sect. 29.4):

$$\Sigma_c(\boldsymbol{r}, \boldsymbol{r}', \varepsilon) = -\int \frac{dv}{2\pi}G_{KS}(\boldsymbol{r}, \boldsymbol{r}', \varepsilon + iv)[W_{KS}(\boldsymbol{r}, \boldsymbol{r}', iv) - v_{ee}(\boldsymbol{r}, \boldsymbol{r}')]. \tag{29.12}$$

Equations (29.10) and (29.11) have a clear OEP-like structure (see Chap. 9) [Krieger 1992b, Grabo 1998]. As a matter of fact, the exact-exchange potential $v_x(\boldsymbol{r}) = \delta E_x[n]/\delta n(\boldsymbol{r})$ also satisfies (29.10) and (29.11) with $\Sigma_c(iu)$ replaced by the exchange-only self-energy:

$$\Sigma_x(\boldsymbol{r}, \boldsymbol{r}') = -\int \frac{dv}{2\pi}\, e^{iv\eta}G_{KS}(\boldsymbol{r}, \boldsymbol{r}', iv)v_{ee}(\boldsymbol{r}, \boldsymbol{r}')$$

$$= -\sum_{j=1}^{N/2}\varphi_j(\boldsymbol{r})\varphi_j^*(\boldsymbol{r}')v_{ee}(\boldsymbol{r}, \boldsymbol{r}'), \tag{29.13}$$

with $\eta \to 0^+$. Moreover, (29.10) for $v_{xc}^{RPA}(\boldsymbol{r}) = v_x(\boldsymbol{r}) + v_c^{RPA}(\boldsymbol{r})$ can be cast in a more familiar form applying $\chi_{KS}(iu = 0)$ on both sides then using (29.4):

$$0 = \int \frac{du}{2\pi}\int d^3r_1 \int d^3r_2 \, G_{KS}(\boldsymbol{r}, \boldsymbol{r}_1, iu)\Big\{\Sigma_{xc}(\boldsymbol{r}_1, \boldsymbol{r}_2, iu)$$

$$- v_{xc}^{RPA}(\boldsymbol{r}_1)\delta(\boldsymbol{r}_1 - \boldsymbol{r}_2)\Big\}G_{KS}(\boldsymbol{r}_2, \boldsymbol{r}, iu), \tag{29.14}$$

where

$$\Sigma_{\mathrm{xc}}(\boldsymbol{r}, \boldsymbol{r}', \varepsilon) = - \int \frac{\mathrm{d}v}{2\pi} \, \mathrm{e}^{\mathrm{i}v\eta} G_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \varepsilon + \mathrm{i}v) W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}v) \,. \qquad (29.15)$$

is the full imaginary-frequency $G_{\mathrm{KS}}W_{\mathrm{KS}}$ self-energy [Hedin 1969]. This equation is known as the linear-response Sham-Schlüter equation [Sham 1983, Sham 1985, Casida 1995b] in the GW approximation for the self-energy.[2]

Solving the linear-response Sham-Schlüter equation is a formidable task. This has nonetheless been done in bulk silicon by Godby et al. [Godby 1986, Godby 1988] and for a jellium surface by Eguiluz et al. [Eguiluz 1992]. An approximate but hopefully reasonnable solution of the linear-response Sham-Schlüter equation [Niquet 2003b, Niquet 2003c, Niquet 2005, Kotani 1998] can be drawn from the static COHSEX approximation to the $G_{\mathrm{KS}}W_{\mathrm{KS}}$ self-energy, that neglects some dynamical contributions to (29.15) [Hedin 1969]. The static COHSEX self-energy splits into a statically screened exchange part Σ_{sex} and a static Coulomb hole term Σ_{coh}:

$$\Sigma_{\mathrm{sex}}(\boldsymbol{r}, \boldsymbol{r}') = - \sum_{j=1}^{N/2} \varphi_j(\boldsymbol{r}) \varphi_j^*(\boldsymbol{r}') W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u = 0) \qquad (29.16\mathrm{a})$$

$$\Sigma_{\mathrm{coh}}(\boldsymbol{r}, \boldsymbol{r}') = \frac{1}{2} \delta(\boldsymbol{r} - \boldsymbol{r}') W_{\mathrm{KS}}^s(\boldsymbol{r}, \boldsymbol{r}, \mathrm{i}u = 0) \,, \qquad (29.16\mathrm{b})$$

where $W_{\mathrm{KS}}^s(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) = W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) - v_{\mathrm{ee}}(\boldsymbol{r}, \boldsymbol{r}')$ is the response part of the RPA screened Coulomb interaction. $\Sigma_{\mathrm{sex}}(\boldsymbol{r}, \boldsymbol{r}')$ has the same functional form as the exchange-only self-energy [(29.13)], but with $v_{\mathrm{ee}}(\boldsymbol{r}, \boldsymbol{r}')$ replaced by $W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u = 0)$. $\Sigma_{\mathrm{coh}}(\boldsymbol{r}, \boldsymbol{r}')$ on the other hand is just half the potential felt by an electron at $\boldsymbol{r}$ and due to the "Coulomb hole" that forms around it (the factor $1/2$ comes from the adiabatic building of this Coulomb hole [Hedin 1969]). Accordingly, the approximate RPA potential that solves (29.14) in the static COHSEX approximation for the self-energy also splits in two parts $\tilde{v}_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r}) = \tilde{v}_{\mathrm{sex}}(\boldsymbol{r}) + \tilde{v}_{\mathrm{coh}}(\boldsymbol{r})$, where $\tilde{v}_{\mathrm{coh}}(\boldsymbol{r}) = \frac{1}{2} W_{\mathrm{KS}}^s(\boldsymbol{r}, \boldsymbol{r}, \mathrm{i}u = 0)$ and $\tilde{v}_{\mathrm{sex}}(\boldsymbol{r})$ satisfies the same equation as the exchange-only potential with $v_{\mathrm{ee}}(\boldsymbol{r}, \boldsymbol{r}')$ replaced by $W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u = 0)$. Therefore $\tilde{v}_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$ can be calculated with any existing x-OEP code once $W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u = 0)$ is known. This has been done by Kotani [Kotani 1998] for example in some bulk metals and silicon.

29.3 Asymptotic Behavior of the RPA Potential in Finite Systems

In this section, we discuss the asymptotic behavior of the RPA potential in finite systems such as atoms. This indeed provides useful insight into the physics of the RPA functional. We focus on the helium atom as a test case.

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[2] Note that the potential is defined by (29.10) and (29.14) up to an additive constant, because $\int \mathrm{d}^3 r \, \chi_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u) = 0$.

Let us first recall the asymptotic behavior ($r \to \infty$) of the *exact* exchange-correlation potential of the He atom [Almbladh 1985]:

$$v_{\mathrm{xc}}(\boldsymbol{r}) = -\frac{1}{r} - \frac{\alpha_{\mathrm{He}^+}}{2r^4} + \mathcal{O}\left(\frac{1}{r^5}\right), \tag{29.17}$$

where $\alpha_{\mathrm{He}^+} = 9/32$ a.u. is the static polarizability of the He$^+$ ion. The $-1/r$ term [that comes from $v_{\mathrm{x}}(\boldsymbol{r})$] is the bare potential felt by an electron dragged away from the He atom, while the $\propto 1/r^4$ term [that comes from $v_{\mathrm{c}}(\boldsymbol{r})$] arises from the polarization of the resulting He$^+$ ion.

We have carefully investigated the asymptotic behavior of the RPA potential in [Niquet 2003b, Niquet 2003c, Niquet 2005]. We find that $v_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$ indeed behaves as (29.17), but with α_{He^+} replaced by the RPA polarizability of the He atom:

$$\alpha_{\mathrm{He}}^{\mathrm{RPA}} = -\int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, z \chi_{\mathrm{RPA}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u = 0) z', \tag{29.18}$$

$\chi_{\mathrm{RPA}}(\mathrm{i}u) = [1 - \chi_{\mathrm{KS}}(\mathrm{i}u)v_{\mathrm{ee}}]^{-1}\chi_{\mathrm{KS}}(\mathrm{i}u)$ being the atomic RPA density-density response function. Note that this result can be (most) easily inferred from a multipole expansion of $W_{\mathrm{KS}}(\boldsymbol{r}, \boldsymbol{r}', \mathrm{i}u)$ in (29.16), $\tilde{v}_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$ having the same asymptotic behavior as $v_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$.

The asymptotic behavior of $v_{\mathrm{x}}(\boldsymbol{r})$ in the exact exchange approximation would be $v_{\mathrm{x}}(\boldsymbol{r}) = -1/r + \mathcal{O}(\exp.)$ [Krieger 1992b, Grabo 1998]. The RPA thus improves over x-OEP in giving the next, $1/r^4$ term of the asymptotic expansion, that accounts for polarization effects. Of course this $1/r^4$ term will not change the long-range behavior of the KS orbitals (as compared to x-OEP), but the underlying physics might still impact the vicinity of the atom. Nonetheless, the $1/r^4$ prefactor, $\alpha_{\mathrm{He}}^{\mathrm{RPA}} = 1.22$ a.u. [van Gisbergen 1998], while consistent with the RPA approximation, is quite far from the expected $\alpha_{\mathrm{He}^+} = 0.28$ a.u. This is reminiscent of the self-correlation problem in the RPA density-density response function and correlation energy: the system still polarizes as a two-electron system upon ionization because (i) the RPA fails to suppress self-correlation and (ii) the RPA fails to account for orbital relaxation. The ACFD-PGG functional, that include exact-exchange effects in two-electron systems, corrects for most of this self-correlation error, yielding $v_{\mathrm{xc}}(\boldsymbol{r}) = -1/r - 0.68/(2r^4) + \mathcal{O}(1/r^5)$ [Niquet 2005]. It still misses orbital relaxation however.

29.4 The Bandgap Energy of Solids

As mentioned in the introduction, DFT, which is a ground-state theory, is not meant for the calculation of quasiparticle band structures. Even the bandgap energy, a linear combination of ground-state total energies, may not be

correctly given by the KS band structure[3] [Sham 1983, Perdew 1982, Perdew 1983, Sham 1985b]. The KS RPA bandgap energies themselves, calculated in $v_{xc}^{RPA}(\boldsymbol{r})$ or $\tilde{v}_{xc}^{RPA}(\boldsymbol{r})$, are too low [Godby 1986, Godby 1988, Kotani 1998]. The quasiparticle band structure of a solid is thus usually computed with the GW method [Hedin 1969, Mattuck 1967]. In principle, the Dyson equation should be solved iteratively to find the self-consistent Green function G and the self-consistent GW self-energy Σ_{xc}. This would notably make the quasiparticle band structure independent of the initial guess for the Green function [Baym 1961, Baym 1962]. Such a self-consistent GW calculation has however long been untractable for real materials. The GW self-energy is thus usually computed using KS orbitals and energies as input. This "$G_{KS}W_{KS}$" approach has been successfully applied to a wide variety of materials [Hybertsen 1985, Hybertsen 1986, Godby 1988, Aulbur 2000]. In most cases it shifts the KS conduction bands with respect to the KS valence bands in a nearly rigid way. It has long been thought that many-body self-consistency would degrade the quality of the GW band structure. The first self-consistent GW calculations in real materials [Schöne 1998, Ku 2002] have however revived this debate and questioned the rationale behind $G_{KS}W_{KS}$ calculations. In this paragraph we show that the RPA functional provides such a rationale within a consistent DFT framework.

The interacting fundamental bandgap energy of a N-electron system is the difference $E_g = I - A$ between its first ionization potential I and its electron affinity A. These are defined as total energy differences between the N- and $(N \pm 1)$-electron systems:

$$I = E(N-1) - E(N) \tag{29.19a}$$
$$A = E(N) - E(N+1) \,. \tag{29.19b}$$

The calculation of I and A as RPA total energy differences yields, after tedious manipulations [Niquet 2004]:

$$-I = \varepsilon_v + \langle \varphi_v | \Sigma_{xc}(\varepsilon_v) - v_{xc}^{RPA} | \varphi_v \rangle + \mathcal{O}(\mathcal{V}^{-1/4}) \tag{29.20a}$$
$$-A = \varepsilon_c + \langle \varphi_c | \Sigma_{xc}(\varepsilon_c) - v_{xc}^{RPA} | \varphi_c \rangle + \mathcal{O}(\mathcal{V}^{-1/4}) \,. \tag{29.20b}$$

$\varphi_v(\boldsymbol{r})$ and $\varphi_c(\boldsymbol{r})$ are the highest occupied and lowest unoccupied orbital KS orbitals, Σ_{xc} is the $G_{KS}W_{KS}$ self-energy[4] [(29.15)] and $\mathcal{V}$ is the volume of the system. Also, one may show [Niquet 2003b] that $\langle \varphi_v | \Sigma_{xc}(\varepsilon_v) - v_{xc}^{RPA} | \varphi_v \rangle = 0$ if the KS potential $v_{KS}(\boldsymbol{r})$ has been shifted so that $\lim_{r \to \infty} v_{KS}(\boldsymbol{r}) = 0$.

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[3] The KS x-OEP bandgap energies of many semiconductors are found to be in good agreement with the experiment [Städele 1997, Städele 1999]. However, the interacting x-OEP bandgap energies of these materials are close to the Hatree-Fock bandgaps and thus too large.

[4] Equation (29.15) is equal to the usual (real-frequency) expression for the $G_{KS}W_{KS}$ self-energy [Hedin 1969] as long as ε is in the KS bandgap (including $\varepsilon = \varepsilon_c$ and $\varepsilon = \varepsilon_v$).

This yields $I = -\varepsilon_{\mathrm{v}} + \mathcal{O}(\mathcal{V}^{-1/4})$: the highest occupied KS energy tends to the negative of the DFT-RPA first ionization potential in bulk systems[5] [Almbladh 1985, Levy 1984]. This result only holds if ε_{v} has been calculated self-consistently [i.e., using $v_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$]; Equations (29.20) remain valid though if LDA/GGA orbitals, energies and potential are used as input for the RPA total energy. The interacting RPA bandgap energy of a solid ($\mathcal{V} \to \infty$) thus differs from the KS RPA bandgap energy $\varepsilon_{\mathrm{g}} = \varepsilon_{\mathrm{c}} - \varepsilon_{\mathrm{v}}$ by a $G_{\mathrm{KS}}W_{\mathrm{KS}}$-like self-energy correction. This shows that the usual $G_{\mathrm{KS}}W_{\mathrm{KS}}$ approach is not a mere practical recipe and that it has a well-defined and meaningful interpretation within DFT. This does not, however, settle the debate about the need and effects of many-body self-consistency.[6] The interacting RPA bandgap energies ($E_{\mathrm{g}} = 1.35$ eV for Si and $E_{\mathrm{g}} = 5.88$ eV for diamond [Niquet 2004]) are usually in reasonnable agreement with the experiment (1.17 eV and 5.48 eV respectively), while the KS RPA bandgap energy of silicon for example is close to the LDA [Godby 1986, Godby 1988, Kotani 1998], showing that the RPA potential has a sizeable derivative discontinuity.

29.5 Conclusion

In this chapter, we have derived the expression of the RPA exchange-correlation potential $v_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$. We have shown that the latter satisfies the so-called linear-response Sham-Schlüter equation in the GW approximation for the self-energy. We have provided an approximate but hopefully reasonnable solution of this equation for practical use. We have then discussed the asymptotic behavior of the RPA potential in finite systems. We have shown that $v_{\mathrm{xc}}^{\mathrm{RPA}}(\boldsymbol{r})$ has the expected $-1/r - \alpha/(2r^4)$ tail in the He atom, though α is the RPA polarizability of He instead of the polarizability of the He$^+$ ion. This is reminiscent of the self-correlation problem in the RPA density-density response function, which can be (partly) corrected in more refined ACFD approximations such as the exact-exchange TD kernel. Last, we have calculated the RPA bandgap energy of a solid. We have shown that the latter differs from the Kohn-Sham bandgap energy by a $G_{\mathrm{KS}}W_{\mathrm{KS}}$-like self-energy correction, computed using Kohn-Sham orbitals and energies as input. This provides a clear rationale behind $G_{\mathrm{KS}}W_{\mathrm{KS}}$ quasiparticle bandgap calculations, that can be consistently interpreted and analyzed within density functional theory.

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[5] Let us recall that $I = -\varepsilon_{\mathrm{v}}$ for the exact exchange-correlation functional provided the external potential $v_{\mathrm{ext}}(\boldsymbol{r}) \to 0$ when $r \to \infty$ [Almbladh 1985, Levy 1984].

[6] There is, moreover, a subtle but important difference between (29.20) and the usual expression for the $G_{\mathrm{KS}}W_{\mathrm{KS}}$ bandgap energy [Hybertsen 1985, Hybertsen 1986, Aulbur 2000]: the former lack the so-called renormalization factors that appear in the latter. The interacting RPA bandgap energies are thus a bit larger than the usual $G_{\mathrm{KS}}W_{\mathrm{KS}}$ figures. A detailed discussion of this point can be found in [Niquet 2004].