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Dependence of Response Functions and Orbital Functionals on Occupation Numbers

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Abstract: Explicitly orbital-dependent approximations to the exchange-correlation energy functional of density functional theory typically not only depend on the single-particle Kohn−Sham orbitals but also on their occupation numbers in the ground-state Slater determinant. The variational calculation of the corresponding exchange-correlation potentials with the optimized effective potential (OEP) method therefore also requires a variation of the occupation numbers with respect to a variation in the effective single-particle potential, which is usually not taken into account. Here it is shown under which circumstances this procedure is justified.

1. Introduction

The central quantity of density functional theory,[1,2] the exchange-correlation energy E_{xc}, is a unique (though unknown) functional of the electron density. Popular approximations such as the local density approximation (LDA) and generalized gradient approximations (GGA's) express E_{xc} as an *explicit* functional of the density.

Recently, another class of approximations has attracted increasing interest: *implicit* density functionals, expressing E_{xc} as explicit functionals of the Kohn−Sham single particle orbitals and energies and therefore only as implicit functionals of the density.[3,4] Members of this class of functionals are the exact exchange functional (EXX), the popular hybrid functionals which mix generalized gradient approximation (GGA) exchange with a fraction of exact exchange,[5−8] the Perdew−Zunger self-interaction correction,[9] and meta-GGA functionals[10−12] which include the orbital kinetic energy density as a key ingredient.

At zero temperature, the orbital functionals mentioned above depend on the occupied orbitals only. Other functionals, such as the second-order correlation energy of Görling−Levy perturbation theory,[13] in addition depend explicitly on the unoccupied orbitals and the orbital energies. Moreover, all these orbital functionals are not only explicit functionals of the orbitals but also explicit functionals of the occupation numbers which, in turn, depend on the single-particle orbital energies. This additional energy dependence is ignored in common implementations of orbital- or energy-dependent functionals.

In order to calculate the single-particle Kohn−Sham potential corresponding to a given orbital functional, the so-called optimized effective potential (OEP) method is used.[3,4,14] The OEP method is a variational method which aims to find that local potential whose orbitals minimize the given total energy expression. In principle, when performing the variation of the local potential, one not only should vary the orbitals but also the orbital energies and occupation numbers. Typically, however, the variation with respect to the occupation numbers is not explicitly performed. In this work, we will investigate when and why this is justified.

2. Density Response Function

In this section, we analyze the problem of the eigenvalue dependence of the occupation numbers in the density and the noninteracting static linear density response function for various situations. We consider the case of zero temperature

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and distinguish between variations at fixed and variable particle number, i.e., for the canonical and grand-canonical ensemble.

2.1. Fixed Particle Number. The density of N noninteracting electrons (at zero temperature) moving in some electrostatic potential $v_s(\mathbf{r})$ is given by

$$n(\mathbf{r}) = \sum_i^{occ} |\varphi_i(\mathbf{r})|^2 \qquad (1)$$

where the single-particle orbitals are solutions of the Schrödinger equation

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right)\varphi_i(\mathbf{r}) = \varepsilon_i \varphi_i(\mathbf{r}) \qquad (2)$$

and the sum in eq 1 runs over the N occupied orbitals of the N-electron Slater determinant. For the ground-state density, one can rewrite eq 1 as

$$n(\mathbf{r}) = \sum_i \theta(\varepsilon_F - \varepsilon_i)|\varphi_i(\mathbf{r})|^2 = \sum_i f_i |\varphi_i(\mathbf{r})|^2 \qquad (3)$$

where the sum now runs over *all* orbitals. ε_F is the Fermi energy, $\theta(x)$ is the Heavyside step function, and $f_i = \theta(\varepsilon_F - \varepsilon_i)$ is the occupation number of orbital $\varphi_i(\mathbf{r})$. It is evident from eq 3 that the density not only depends on the (occupied) orbitals $\varphi_i(\mathbf{r})$ but also on the orbital energies ε_i, since the very specification of which orbitals are occupied and which unoccupied depends on their energies.

Through eq 2, both of these quantities are functionals of the potential $v_s(\mathbf{r})$, i.e., $\varphi_i(\mathbf{r}) = \varphi_i[v_s](\mathbf{r})$, $\varepsilon_i = \varepsilon_i[v_s]$. The static density response function, which is the functional derivative of n with respect to v_s, is therefore given as

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}') = \frac{\delta n(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \sum_i \frac{\delta f_i}{\delta v_s(\mathbf{r}')}|\varphi_i(\mathbf{r})|^2 + \chi(\mathbf{r}, \mathbf{r}') \qquad (4)$$

with

$$\chi(\mathbf{r}, \mathbf{r}') = \sum_i f_i \left(\frac{\delta \varphi_i(\mathbf{r})}{\delta v_s(\mathbf{r}')}\varphi_i^*(\mathbf{r}) + c.c.\right)$$
$$= \sum_{\substack{i,k \\ i \neq k}} f_i \left(\frac{\varphi_k^*(\mathbf{r})\varphi_k(\mathbf{r}')\varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}')}{\varepsilon_i - \varepsilon_k} + c.c.\right) \qquad (5)$$

The last step follows from first order perturbation theory, which can be used to obtain

$$\frac{\delta \varphi_i(\mathbf{r})}{\delta v_s(\mathbf{r}')} = \sum_{\substack{k \\ k \neq i}} \frac{\varphi_k(\mathbf{r})\varphi_k^*(\mathbf{r}')\varphi_i(\mathbf{r}')}{\varepsilon_i - \varepsilon_k} \qquad (6)$$

For simplicity, we have assumed a nondegenerate single-particle spectrum.

Usually, $\chi(\mathbf{r}, \mathbf{r}')$ of eq 5 is taken as the static density response function instead of $\tilde{\chi}$. Both expressions differ by the first term on the right-hand side of eq 4, becoming identical only if this term vanishes. In order to see when and how this happens we consider two cases.

Case 1 comprises systems for which the single-particle spectrum has a finite gap between the highest occupied orbital (eigenvalue ε_N) and the lowest unoccupied orbital (eigenvalue ε_{N+1}). Then, the Fermi energy ε_F lies strictly between these

two orbital energies, $\varepsilon_N < \varepsilon_F < \varepsilon_{N+1}$. Within the single-particle gap, the position of ε_F is arbitrary (at zero temperature). The important point now is that upon (infinitesimal) variation of the potential v_s, ε_F remains fixed and does not need to be varied. The reason is that the variation $\delta\varepsilon_N$ of ε_N due to the variation of v_s is infinitesimal as well and ε_F can be chosen such that $\varepsilon_F > \varepsilon_N + \delta\varepsilon_N$, thus leaving the particle number unchanged. Then the functional derivative of the occupation number with respect to v_s becomes

$$\frac{\delta f_i}{\delta v_s(\mathbf{r})} = \frac{\partial \theta(\varepsilon_F - \varepsilon_i)}{\partial \varepsilon_i}\frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} = -\delta(\varepsilon_F - \varepsilon_i)|\varphi_i(\mathbf{r})|^2 \qquad (7)$$

where $\delta(x)$ is the Dirac delta function, and we used the relation

$$\frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} = |\varphi_i(\mathbf{r})|^2 \qquad (8)$$

which can be obtained from first-order perturbation theory. In the present case, the Fermi energy (which is in the single-particle gap) is not equal to any of the single-particle energies, the delta function in eq 7 vanishes, and $\tilde{\chi}(\mathbf{r}, \mathbf{r}')$ of eq 4 coincides with the usual form of the static density response function of eq 5.

Case 2 is the case of a vanishing single-particle gap, i.e., the case of an open-shell or metallic system. For notational simplicity, in the following discussion, we still work with the assumption of a nondegenerate single-particle spectrum. Of course, particularly for open-shell systems, this assumption is inappropriate. The more general case including degenerate single-particle orbitals is discussed in the Appendix.

The crucial difference to case 1 is that an infinitesimal variation of the potential v_s now not only leads to a variation $\delta\varepsilon_i$ of the single-particle energies but also to a variation $\delta\varepsilon_F$ of the Fermi energy. This latter variation has to be taken into account in order for the particle number to be conserved (i.e., the infinitesimal variation δN of the particle number upon variation of the potential strictly has to vanish, $\delta N = 0$). Then, the functional derivative of the occupation number with respect to the potential consists of two terms and reads

$$\frac{\delta f_i}{\delta v_s(\mathbf{r})} = \frac{\partial \theta(\varepsilon_F - \varepsilon_i)}{\partial \varepsilon_F}\frac{\delta \varepsilon_F}{\delta v_s(\mathbf{r})} + \frac{\partial \theta(\varepsilon_F - \varepsilon_i)}{\partial \varepsilon_i}\frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} \qquad (9)$$
$$= \delta(\varepsilon_F - \varepsilon_i)(|\varphi_F(\mathbf{r})|^2 - |\varphi_i(\mathbf{r})|^2)$$

where φ_F is the highest occupied orbital with orbital energy equal to the Fermi energy. Due to the delta function, the right-hand side (rhs) of eq 9 vanishes and again $\tilde{\chi}(\mathbf{r}, \mathbf{r}')$ of eq 4 coincides with the static density response function $\chi(\mathbf{r}, \mathbf{r}')$ of the form given in eq 5.

From eq 4, the linear change in the density due to the perturbation $\delta v_s(\mathbf{r})$ is $\delta n(\mathbf{r}) = \int d^3r' \, \tilde{\chi}(\mathbf{r}, \mathbf{r}')\delta v_s(\mathbf{r}')$. One can then check explicitly that the result $\tilde{\chi}(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}, \mathbf{r}')$ obtained here is fully consistent with a fixed number of particles:

$$\delta N = \int d^3r \, \delta n(\mathbf{r}) = \int d^3\mathbf{r}' \, \delta v_s(\mathbf{r}')\int d^3r \, \tilde{\chi}(\mathbf{r}, \mathbf{r}')$$
$$= \int d^3\mathbf{r}' \, \delta v_s(\mathbf{r}')\int d^3r \, \chi(\mathbf{r}, \mathbf{r}') = 0 \qquad (10)$$

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where the last equality follows from the orthonormality of the single-particle orbitals.

We note that the problem we are discussing here involves the response function $(\delta n[v_s])/(\delta v_s)$ itself and is thus conceptually distinct from the question of invertibility of this response function, which appears when the single-particle potentials are not uniquely determined by the densities.[15]

2.2. Grand Canonical Ensemble. The analysis is slightly altered if the system of noninteracting electrons is connected to a particle bath, i.e., for the grand canonical ensemble characterized by a chemical potential μ. The density (at zero temperature) is then given by

$$n(\mathbf{r}) = \sum_i \theta(\mu - \varepsilon_i)|\varphi_i(\mathbf{r})|^2 = \sum_i f_i|\varphi_i(\mathbf{r})|^2 \quad (11)$$

where the occupation number now is given by $f_i = \theta(\mu - \varepsilon_i)$ and the sum again runs over all single-particle orbitals. When varying the occupation numbers with respect to variations of the potential, the chemical potential remains constant, independent of the single-particle spectrum having a finite or vanishing gap at μ. The variation of f_i then is obtained similarly to case 1 of the previous subsection as

$$\frac{\delta f_i}{\delta v_s(\mathbf{r})} = \frac{\partial \theta(\mu - \varepsilon_i)}{\partial \varepsilon_i} \frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} = -\delta(\mu - \varepsilon_i)|\varphi_i(\mathbf{r})|^2 \quad (12)$$

This term does not vanish if the chemical potential is aligned with one of the single-particle energies, and the static density response function for the grand-canonical ensemble reads

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}, \mathbf{r}') - \sum_i \delta(\mu - \varepsilon_i)|\varphi_i(\mathbf{r})|^2|\varphi_i(\mathbf{r}')|^2 \quad (13)$$

It is worth noting that now, due to the second term on the rhs of eq 13, δN (eq 10) is different from zero which is of course consistent with the fact that here we are dealing with an open system.

3. Implications for the Optimized Effective Potential

The central idea of density functional theory is to write the ground-state energy E_{tot} of N interacting electrons moving in an external potential $v_0(\mathbf{r})$ as a functional of the ground-state density. This energy functional may then be split into various pieces as

$$E_{tot} = T_s[n] + \int d^3r \, v_0(\mathbf{r})n(\mathbf{r}) + U[n] + E_{xc}[n] \quad (14)$$

where $T_s[n]$ is the kinetic energy functional of *noninteracting* electrons,

$$U[n] = \frac{1}{2} \int d^3r \int d^3r' \frac{n(\mathbf{r})n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \quad (15)$$

is the classical electrostatic energy, and E_{xc} is the exchange-correlation energy functional which incorporates all complicated many-body effects and in practice has to be approximated. Minimization of eq 14 with respect to the density leads to an effective single-particle equation of the form of eq 2 where the effective potential is

$$v_s(\mathbf{r}) = v_0(\mathbf{r}) + \int d^3r' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} + v_{xc}(\mathbf{r}) \quad (16)$$

with the exchange-correlation potential

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} \quad (17)$$

While the most popular approximations to the exchange-correlation energy E_{xc} are explicit functionals of the density, there has been increasing interest in another class of approximations which are are only *implicit* functionals of the density. These functionals instead depend explicitly on the Kohn–Sham single-particle orbitals as well as on the Kohn–Sham orbital energies. One example for such a functional is the exact exchange energy given as

$$E_x^{EXX} = -\frac{1}{4} \int d^3r \int d^3r' \frac{|\gamma(\mathbf{r}, \mathbf{r}')|^2}{|\mathbf{r} - \mathbf{r}'|} \quad (18)$$

where

$$\gamma(\mathbf{r}, \mathbf{r}') = \sum_i f_i \varphi_i(\mathbf{r})\varphi_i^*(\mathbf{r}') \quad (19)$$

is the single-particle density matrix. As one can see, E_x^{EXX} depends on the single-particle energies through the occupation numbers f_i. Other functionals such as, e.g., the correlation energy functional of second-order Görling–Levy perturbation theory,[13] depend on the orbital energies also in other ways (see below).

In order to distinguish a genuine dependence on orbital energies from a dependence on occupation numbers, we write for a general exchange-correlation energy functional $E_{xc} = E_{xc}[\{\varphi_i\}, \{\varepsilon_i\}, \{f_i\}]$. The exchange-correlation potential of such a functional can be computed by using the chain rule of functional differentiation as

$$v_{xc}(\mathbf{r}) = \frac{\delta E_{xc}}{\delta n(\mathbf{r})} = \int d^3\mathbf{r}' \frac{\delta E_{xc}}{\delta v_s(\mathbf{r}')} \frac{\delta v_s(\mathbf{r}')}{\delta n(\mathbf{r})} \quad (20)$$

Acting with the density response operator (eq 4) on both sides of this equation, one arrives at

$$\int d^3\mathbf{r}' \, v_{xc}(\mathbf{r}')\tilde{\chi}(\mathbf{r}', \mathbf{r}) = \frac{\delta E_{xc}}{\delta v_s(\mathbf{r})}$$

$$= \sum_i \int d^3\mathbf{r}' \left(\left(\frac{\delta E_{xc}}{\delta \varphi_i(\mathbf{r}')} \bigg|_{\{\varepsilon_k\}, \{f_k\}} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + c.c. \right) + \right.$$

$$\left. \frac{\partial E_{xc}}{\partial \varepsilon_i} \bigg|_{\{\varphi_k\}, \{f_k\}} \frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} + \frac{\partial E_{xc}}{\partial f_i} \bigg|_{\{\varphi_k\}, \{\varepsilon_k\}} \frac{\delta f_i}{\delta v_s(\mathbf{r})} \right) \quad (21)$$

In the last step, we have used the chain rule once again and we also emphasize in the notation that when varying with respect to one set of variables (orbitals, orbital energies, or occupation numbers) the other variables remain fixed.

Equation 21 is the OEP integral equation in its general form. For a given approximate E_{xc}, this equation *defines* the corresponding $v_{xc}(\mathbf{r})$ and has to be solved in a self-consistent way together with the Kohn–Sham equations (eq 2). It differs in three ways from the form most commonly found in the literature (see, e.g., refs 3 and 4 and references therein). One, the explicit energy dependence is handled in a similar way as is the orbital dependence, via the chain rule. The other two arise from the implicit energy dependence of the occupation numbers and are our main concern here. Similar

to the discussion in the previous section, we will again distinguish between the two cases of fixed particle number and systems in contact with a particle bath and discuss the role of these extra terms in both cases.

3.1. Fixed Particle Number. As we have seen in section 2, for the case of fixed particle number at zero temperature, the functional derivative $\delta f_i/\delta v_s(\mathbf{r})$ vanishes both for systems with a finite and vanishing HOMO−LUMO gap. This has two consequences for eq 21: first, we can replace the response function $\tilde{\chi}$ by the function χ of eq 5, and second, the last term on the rhs of eq 21 drops out. Therefore, the OEP equation reads

$$\int d^3 r' \, v_{xc}(\mathbf{r}')\chi(\mathbf{r}', \mathbf{r})$$
$$= \sum_i \left[\int d^3 r' \left(\frac{\delta E_{xc}}{\delta \varphi_i(\mathbf{r}')} \Big|_{\{\varepsilon_k\},\{f_k\}} \frac{\delta \varphi_i(\mathbf{r}')}{\delta v_s(\mathbf{r})} + \text{c.c.} \right) + \frac{\partial E_{xc}}{\partial \varepsilon_i} \Big|_{\{\varphi_k\},\{f_k\}} \frac{\delta \varepsilon_i}{\delta v_s(\mathbf{r})} \right] \quad (22)$$

This equation shows that despite the dependence of E_{xc} on the occupation numbers (which, in turn, depend on the orbital energies), the variation with respect to these occupation numbers may be omitted for the calculation of the OEP integral equation for the exchange-correlation potential. This is, of course, what has been done in the vast majority of cases discussed in the literature.

We note in passing that integrating eq 22 over all space and using the orthornormality of the Kohn−Sham orbitals one can deduce the sum rule[16]

$$\sum_i \frac{\partial E_{xc}}{\partial \varepsilon_i} \Big|_{\{\varphi_k\},\{f_k\}} = 0 \quad (23)$$

On quite general grounds, one expects that for an isolated system with a fixed number of particles, $v_{xc}(\mathbf{r})$ is only defined up to a constant. To check if eq 22 meets this condition, we need an explicit expression for E_{xc}. As a nontrivial example, we use

$$E_{xc} \approx E_x^{EXX} + E_c^{(2)} \quad (24)$$

where E_x^{EXX} is the exact exchange energy of eq 18 and $E_c^{(2)}$ is the second-order correlation energy of Görling−Levy perturbation theory[13,17,18] defined by

$$E_c^{(2)} = E_{c,1} + E_{c,2} \quad (25)$$

where

$$E_{c,1} = \sum_{i,j} \frac{f_i(1-f_j)}{(\varepsilon_i - \varepsilon_j)} \left| \langle i|v_x|j \rangle + \sum_k f_k(ik\|kj) \right|^2 \quad (26)$$

and

$$E_{c,2} = \frac{1}{2} \sum_{i,j,k,l} \frac{f_i f_j (1-f_k)(1-f_l)}{(\varepsilon_i + \varepsilon_j - \varepsilon_k - \varepsilon_l)} (ij\|kl)[(kl\|ij) - (kl\|ji)] \quad (27)$$

In the equations above, we have used the notations

$$(ij\|kl) = \int d^3 r \int d^3 r' \frac{\varphi_i^*(\mathbf{r})\varphi_k(\mathbf{r})\varphi_j^*(\mathbf{r}')\varphi_l(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad (28)$$

and

$$\langle i|v_x|j \rangle = \int d^3 r \, \varphi_i^*(\mathbf{r})v_x(\mathbf{r})\varphi_j(\mathbf{r}) \quad (29)$$

Suppose now that we introduce a rigid shift $v_s(\mathbf{r}) \to v_s(\mathbf{r}) + C$ in the effective single particle potential of eq 2. As a result, if $\{\varphi_i\}$, $\{\varepsilon_i\}$, $\{f_i\}$ are a set of solutions for $v_s(\mathbf{r})$, the solutions for $v_s(\mathbf{r}) + C$ are $\{\varphi_i\}$, $\{\varepsilon_i + C\}$, $\{f_i\}$. This holds provided that eq 22 determines $v_{xc}(\mathbf{r})$ only up to a constant. Inspection of eq 18 confirms that this is the case: the left-hand side (lhs) is invariant under a rigid shift of $v_{xc}(\mathbf{r})$, and eqs 18 and 25 are invariant under the change $\{\varepsilon_i\} \to \{\varepsilon_i + C\}$.

3.2. Grand Canonical Ensemble. The situation is different if the system is in contact with a particle bath. Since in this case $\delta f_i/\delta v_s(\mathbf{r})$ does not vanish one has to use the full OEP eq 21. Here, the dependence of both the density and the exchange-correlation energy on the occupation numbers has to be taken into account explicitly when performing the variations and the two extra terms resulting from this variation cannot be neglected. Applications of this OEP formalism for open systems have been reported for quasi-two-dimensional electron gases (2DEG) in *n*-doped semiconductor quantum wells where the *n*-doped regions act as particle reservoirs.[19−21] A qualitative discussion of the importance of the extra terms for the particular case of 2DEG can be found in the discussion of eqs 6−8 of ref 21.

As another consequence of the extra terms, integration of eq 21 over all space leads to the modified sum rule

$$-\sum_i \delta(\mu - \varepsilon_i)\bar{v}_{xc,i}$$
$$= \sum_i \left(\frac{\partial E_{xc}}{\partial \varepsilon_i} \Big|_{\{\varphi_k\},\{f_k\}} - \frac{\partial E_{xc}}{\partial f_i} \Big|_{\{\varphi_k\},\{\varepsilon_k\}} \delta(\mu - \varepsilon_i) \right) \quad (30)$$

where

$$\bar{v}_{xc,i} = \int d^3 r \, v_{xc}(\mathbf{r})|\varphi_i(\mathbf{r})|^2 \quad (31)$$

We take the exact exchange functional (eq 18) as an example for a functional which does not explicitly depend on the single-particle energies. In this case, the first term on the rhs of eq 30 vanishes. If there exists a single-particle state whose energy equals the chemical potential, $\varepsilon_N = \mu$, we then obtain

$$\bar{v}_{x,N}^{EXX} = \frac{\partial E_x^{EXX}}{\partial f_N} \quad (32)$$

This relation is the complete analogue for the grand canonical ensemble of a well-known relation for fixed particle number which reads[22−24]

$$\bar{v}_{x,N}^{EXX} = \bar{u}_{x,N}^{EXX} \quad (33)$$

where

$$\bar{u}_{x,N}^{EXX} = \frac{1}{f_N} \int d^3 r \, \varphi_N(\mathbf{r}) \frac{\delta E_x^{EXX}}{\delta \varphi_N(\mathbf{r})} \quad (34)$$

For open 2DEG's, this relation has been obtained previously by studying the asymptotic behavior of the exact-exchange potential.[20]

For the grand-canonical ensemble, $v_{xc}(\mathbf{r})$ is *fully determined* by eq 21 since this equation is *not* invariant under a rigid shift of the potential: the lhs is not invariant due to the

extra term in $\tilde{\chi}(\mathbf{r}, \mathbf{r}')$ in eq 13. The rhs is not invariant because E_{xc} changes under the transformation $\{\varepsilon_i\} \rightarrow \{\varepsilon_i + C\}$. This is due to the fact that the chemical potential μ (which is determined by the particle reservoirs) remains fixed in the grand canonical ensemble and the above transformation leads to a change in the set of occupation numbers and self-consistent KS orbitals, $\{f_i\}$ and $\{\varphi_i\}$, respectively. This is consistent with the result of Argaman and Makov[25] who showed that in a grand-canonical ensemble the single-particle potentials are uniquely determined by the densities.

4. Conclusions

In this work, we have addressed the question why and when one can ignore the explicit dependence on the orbital occupation numbers (which in turn depend explicitly on the orbital energies) when calculating both the static linear density response function and the effective single-particle potential corresponding to an orbital-dependent exchange-correlation energy functional. We have shown that the variation of the occupation numbers may safely be neglected for systems with fixed particle number. For systems connected to a particle bath, however, this variation leads to nonvanishing contributions and needs to be taken into account.

Appendix: Degenerate Single-Particle Spectrum

In general, the single-particle spectrum will have eigenvalues which may be degenerate. In particular, in the case of open-shell systems, the energy of the highest occupied orbital is degenerate and the arguments of case 2 discussed in section 2.1 need to be modified.

As degeneracy is in almost all cases related to symmetry, we will use the language of group theory. In particular, the single-particle orbitals will be labeled by a complete set of quantum numbers $\{n, l, m\}$ where n is the principal quantum number (which is not related to symmetry), l is a label denoting the irreducible representation of the symmetry group $\mathscr{G}$ of the single-particle potential $v_s(\mathbf{r})$, and m labels a partner within that representation. The single-particle equation now reads

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r})\right)\varphi_{nlm}(\mathbf{r}) = \varepsilon_{nl}\varphi_{nlm}(\mathbf{r}) \tag{35}$$

and it should be noted that the eigenvalue ε_{nl} is independent of the partner label m. Furthermore, writing the energy eigenvalue as a functional of the potential, $\varepsilon_{nl}[v_s]$, one has to keep in mind that this functional is only well defined for potentials which are invariant under the transformations of

the symmetry group $\mathscr{G}$ because l refers to an irreducible representation of that group. Therefore, we calculate the variation of the orbital energies, $\delta\varepsilon_{nl} = \varepsilon_{nl}[v_s + \delta v_s] - \varepsilon_{nl}[v_s]$ resulting from a variation $\delta v_s(\mathbf{r})$ which preserves the symmetry of $v_s(\mathbf{r})$. Replacing $v_s \rightarrow v_s + \delta v_s$, $\varphi_{nlm} \rightarrow \varphi_{nlm} + \delta\varphi_{nlm}$, in eq 35, one finds that the first-order change in the energy eigenvalue is given by

$$\delta\varepsilon_{nl} = \int d^3r \, |\varphi_{nlm}(\mathbf{r})|^2 \delta v_s(\mathbf{r}) \tag{36}$$

Summing this equation over the partner label m one obtains

$$d_{nl}\delta\varepsilon_{nl} = \int d^3r \sum_m |\varphi_{nlm}(\mathbf{r})|^2 \delta v_s(\mathbf{r}) \tag{37}$$

where d_{nl} is the degeneracy of ε_{nl}. Now, we note that the single-particle orbitals $\varphi_{nlm}(\mathbf{r})$ may be written as

$$\varphi_{nlm}(\mathbf{r}) = R_{nl}(\mathbf{r})X_{lm}(\mathbf{r}) \tag{38}$$

where $R_{nl}(\mathbf{r})$ is a totally symmetric function which is invariant under all symmetry transformations T of the group $\mathscr{G}$ and $X_{lm}(\mathbf{r})$ is a function which transforms according to the irreducible representation l of $\mathscr{G}$, i.e.,

$$X_{lm}(R^{-1}(T)\mathbf{r}) = \sum_{m'} \Gamma^{(l)}(T)_{m'm}X_{lm'}(\mathbf{r}) \tag{39}$$

Here, $R(T)$ is a 3×3 matrix describing the symmetry operation $T \in \mathscr{G}$ in three-dimensional space and $\Gamma^{(l)}(T)$ is the representation matrix of group element T in the irreducible representation l of $\mathscr{G}$. Noting now that $\sum_m |X_{lm}(\mathbf{r})|^2$ is a totally symmetric function, we find for the functional derivative

$$\frac{\delta\varepsilon_{nl}}{\delta v_s(\mathbf{r})} = |\tilde{R}_{nl}(\mathbf{r})|^2 \tag{40}$$

where we have defined

$$\tilde{R}_{nl}(\mathbf{r}) = \frac{1}{\sqrt{d_{nl}}}R_{nl}(\mathbf{r})\sqrt{\sum_m |X_{lm}(\mathbf{r})|^2} \tag{41}$$

which is again invariant under all symmetry transformations of the group $\mathscr{G}$.

Equation 40 will shortly be used to repeat the arguments of section 2.1 for the degenerate, open-shell case. Before we do so, we point out that the definition of the density of eq 3 needs to be modified because not all orbitals with energy ε_F are (fully) occupied. This can be achieved, e.g., by writing the density as

$$n(\mathbf{r}) = \sum_{n,l,m} f_{nlm}|\varphi_{nlm}(\mathbf{r})|^2 \tag{42}$$

and occupying all degenerate orbitals of the partially filled subshell with the same fractional number of electrons, i.e., by defining the occupation number of the partially filled subshell by $f_{nlm} = f_{nl} = (n_{nl}/d_{nl})\theta(\varepsilon_F - \varepsilon_{nl})$ where n_{nl} is the number of electrons in the open subshell. With this definition, the static density response function reads

$$\tilde{\chi}(\mathbf{r}, \mathbf{r}') = \chi(\mathbf{r}, \mathbf{r}') + \sum_{n,l,m} \frac{\delta f_{nl}}{\delta v_s(\mathbf{r})}|\varphi_{nlm}(\mathbf{r})|^2 \tag{43}$$

with

$$\chi(\mathbf{r}, \mathbf{r}') = \sum_{\substack{n,l,m \\ n',l',m' \\ \varepsilon_{nl} \neq \varepsilon_{n'l'}}} f_{nl}\left(\frac{\varphi_{n'l'm'}^*(\mathbf{r})\varphi_{n'l'm'}(\mathbf{r}')\varphi_{nlm}(\mathbf{r})\varphi_{nlm}^*(\mathbf{r}')}{\varepsilon_{nl} - \varepsilon_{n'l'}} + \text{c.c.}\right)$$

$$(44)$$

and

$$\frac{\delta f_{nl}}{\delta v_s(\mathbf{r})} = \frac{n_{nl}}{d_{nl}}\delta(\varepsilon_F - \varepsilon_{nl})(|\tilde{R}_F(\mathbf{r})|^2 - |\tilde{R}_{nl}(\mathbf{r})|^2) = 0 \quad (45)$$

where the last equality follows because the total symmetric part of degenerate orbitals is identical. Therefore, just as in the nondegenerate case at fixed particle number, the functional derivative with respect to the occupation numbers may be neglected both in the calculation of the density response function as well as in the derivation of the OEP equation.

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