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Polarizability from occupied wavefunctions

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Abstract. An expression for the static polarizability of a system of electrons moving in an external potential is obtained in terms of occupied wavefunctions of a single-particle Hamiltonian. The formalism is exact within the density functional theory. For a single electron in an external potential the polarizability is expressed in terms of the ground-state charge density.

1. Introduction

In linear response theory the static polarizability, $\chi(r, r')$, determines the response of the charge density of a system of electrons to a static external perturbation, and hence χ describes the screening properties of the electrons. In the Adler-Wieser formulation [1] of the random phase approximation (RPA), the evaluation of the polarizability requires an accurate set of eigenvalues and eigenstates, both for the occupied states as well as the empty states. An analytic expression for the RPA polarizability of the homogeneous electron gas is known, but the best that can usually be done for an inhomogeneous system is to express the independent-particle polarizability in terms of an infinite sum over products of occupied and empty states. It is straightforward to formally include exchange–correlation effects [2] and hence to go beyond the RPA within density functional theory (DFT) [3], but the RPA polarizability still has to be calculated.

The static polarizability is a ground-state property and hence a functional of the ground-state charge density [4]. In principle, one should therefore be able to determine the static polarizability from a knowledge of the ground-state charge density, but since the exact functional dependence of the polarizability on the charge density is not known this remains a formality. Stoddart and Hanks [5], however, examined the relationship between a perturbative expansion of the kinetic and exchange–correlation energy functionals and the electronic response functions. This approach makes use of the dependence of the static response functions on the ground-state charge density, but is limited by the incomplete knowledge of the energy functionals. Another attempt along these lines was made by Car and co-workers [6], but again the formalism is limited because of lack of information about energy functionals.

In an alternative approach the inverse dielectric function can be determined directly by relating the change in the self-consistent single-electron potential in response to small perturbations of the external potential to the perturbing

potential [2, 7]. Implicit in this approach is the dependence of the dielectric function on the ground-state charge density. However, since in this method the effective single-particle potential has to be calculated self-consistently for different external potentials, it has until now only been applied to a limited number of highly symmetrical situations.

Within density functional theory it is a simple matter to calculate the single-particle states for an effective single-particle Hamiltonian. The ground-state charge density is then expressed in terms of the occupied wave functions. It would be worthwhile to have an expression for the polarizability in terms of the occupied wavefunctions, which can in general be calculated more accurately than the infinite number of unoccupied states.

In this paper we take another look at ways to express the static polarizability and derive an expression for the polarizability in terms of the occupied wavefunctions of an independent-particle Hamiltonian. The formalism is exact within DFT.

The organization of the paper is as follows. In section 2 the formal dependence of the static polarizability on the ground-state charge density is examined and some general properties of χ are discussed. Section 3 deals with the case of a single electron, and an expression for the polarizability of the hydrogen atom in terms of the ground-state charge density is derived. In section 4 an expression for the independent-particle polarizability in terms of the occupied wavefunctions in an independent-particle formalism is derived. Finally, in section 4, concluding remarks are given.

2. Static polarizability

The polarizability of the electrons relates a small perturbation in the external potential to the resulting change in the electron charge density. For static perturbations we have

$$\delta\rho(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta v_{\text{ext}}(\mathbf{r}') d\mathbf{r}'. \quad (1)$$

In a single-particle description of a system of electrons moving in an external potential, the single-particle Hamiltonian is usually expressed in terms of an effective potential $v_{\text{eff}}(\mathbf{r})$:

$$H = -\frac{1}{2}\nabla^2 + v_{\text{eff}}(\mathbf{r}) \quad (2)$$

with

$$v_{\text{eff}}(\mathbf{r}) = v_{\text{sc}}(\mathbf{r}) + v_{\text{ext}}(\mathbf{r}) \quad (3)$$

where $v_{\text{sc}}(\mathbf{r})$ must be determined self-consistently. For a solid it would be appropriate to use density functional theory [3] with

$$v_{\text{sc}}(\mathbf{r}) = v_{\text{H}}(\mathbf{r}) + v_{\text{xc}}(\mathbf{r}) \quad (4)$$

where $v_{\text{H}}(\mathbf{r})$ is the Hartree potential and $v_{\text{xc}}(\mathbf{r})$ is the exchange-correlation potential. The single-particle eigenstates, $\psi_n(\mathbf{r})$, and eigenenergies, ϵ_n , are defined by the Hamiltonian H :

$$H\psi_n(\mathbf{r}) = \epsilon_n\psi_n(\mathbf{r}). \quad (5)$$

The ground-state charge density, $\rho(\mathbf{r})$, can be expressed as

$$\rho(\mathbf{r}) = \sum_n^{\text{occ}} |\psi_n(\mathbf{r})|^2 \quad (6)$$

and the ground-state energy of the electrons, $E_{\text{el}}[\rho]$, as

$$E_{\text{el}}[\rho] = T[\rho] + \int \rho(\mathbf{r}) v_{\text{eff}}(\mathbf{r}) d\mathbf{r} + \Delta E_c[\rho] = F[\rho] + \int \rho(\mathbf{r}) v_{\text{ext}}(\mathbf{r}) d\mathbf{r}. \quad (7)$$

Here $\Delta E_c[\rho]$ takes care of double-counting terms and corrections to the exchange-correlation energy contribution from the independent-particle expression. In the last line of (7), $F[\rho]$ is the energy functional consisting of the kinetic energy, $T[\rho]$, of a non-interacting electron gas of density ρ , and the interaction energy of the electrons of density ρ in the approximation which leads to v_{sc} .

If we assume a non-degenerate ground state, $E[\rho]$ is a unique functional of ρ and is a minimum for the correct ground-state charge density. The variation of $E[\rho]$ with respect to fluctuations in ρ around the ground-state charge density, ρ_0 , is therefore zero. With each charge density ρ , we associate a unique (up to a constant) external potential v_{ext} . Now consider a small perturbation in the charge density. Let ρ_0 be the charge density of the unperturbed system, and $\rho = \rho_0 + \delta\rho$ (with $\int \delta\rho(\mathbf{r}) d\mathbf{r} = 0$) that of the perturbed system. The fluctuation $\delta\rho$ is associated with a unique change, δv_{ext} , of v_{ext} . We therefore have a unique relationship between ρ_0 and v_{ext}^0 and between ρ and $v_{\text{ext}} = v_{\text{ext}}^0 + \delta v_{\text{ext}}$. The change in $E[\rho]$, to second order in $\delta\rho$ [4], is given by

$$\begin{aligned} \Delta E_{\text{el}} = & \int \delta v_{\text{ext}}(\mathbf{r}) [\rho_0(\mathbf{r}) + \delta\rho(\mathbf{r})] d\mathbf{r} + \int \left[v_{\text{ext}}^0(\mathbf{r}) + \frac{\delta F}{\delta\rho(\mathbf{r})} \right]_{\rho_0} \delta\rho(\mathbf{r}) d\mathbf{r} \\ & + \frac{1}{2} \int \int \frac{\delta^2 F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \Big|_{\rho_0} \delta\rho(\mathbf{r})\delta\rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \end{aligned} \quad (8)$$

The functional derivatives are determined at $\rho = \rho_0$. Because of the minimal property of $E_{\text{el}}[\rho]$ for the unperturbed system, the second integral vanishes. Applying the minimal property to the perturbed system leads to the condition

$$\delta v_{\text{ext}}(\mathbf{r}) = - \int \frac{\delta^2 F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \Big|_{\rho_0} \delta\rho(\mathbf{r}') d\mathbf{r}'. \quad (9)$$

Inverting this equation we get

$$\delta\rho(\mathbf{r}) = \int \left[- \frac{\delta^2 F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \Big|_{\rho_0} \right]^{-1} \delta v_{\text{ext}}(\mathbf{r}') d\mathbf{r}'. \quad (10)$$

Thus $[-\delta^2 F/\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')]_{\rho_0}^{-1}$ relates a perturbation in the external potential to the linear change in the charge density, and therefore this expression must be equivalent to the polarizability of the electrons:

$$\chi(\mathbf{r}, \mathbf{r}') = \left[- \frac{\delta^2 F}{\delta\rho(\mathbf{r})\delta\rho(\mathbf{r}')} \Big|_{\rho_0} \right]^{-1}. \quad (11)$$

Strictly speaking neither $[\delta^2 F / \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')]]$ nor χ has an inverse. Both, however, are real symmetric matrices and hence Hermitian operators. They can therefore be expressed in terms of a complete set of eigenvectors and eigenvalues. For χ we have

$$\begin{aligned} \chi |n\rangle &= \chi_n |n\rangle \\ \chi &= \sum_n |n\rangle \chi_n \langle n|. \end{aligned} \quad (12)$$

Because every external potential (up to a constant) defines a unique charge density, for every perturbation δv_{ext} there is an associated charge fluctuation. However, since a change in potential that is constant over all space cannot alter the charge distribution, we have that

$$\delta \rho = \chi (\delta v_{\text{ext}} + \lambda) = \chi \delta v_{\text{ext}} \quad (13)$$

where λ is a constant. This implies that χ has a null vector, i.e. at least one of the eigenvalues χ_n must be zero, and consequently the inverse of χ does not exist. Because of the unique relationship between the charge density and the external potential, for every δv_{ext} with $\int \delta v_{\text{ext}}(\mathbf{r}) d\mathbf{r} = 0$, a unique non-zero charge fluctuation can be associated. This implies that for each perturbation $\delta v_{\text{ext}} = |n\rangle$ for which $\int \langle \mathbf{r} | n \rangle d\mathbf{r} = 0$, a non-zero fluctuation $\delta \rho$ exists and consequently the associated eigenvalue χ_n must be non-zero. Any eigenvector $|n\rangle$ of χ for which $\int \langle \mathbf{r} | n \rangle d\mathbf{r} \neq 0$, of which there must be at least one, must therefore belong to the null space of χ . The inverse of χ exists in the space spanned by functions with the property that the integral over all space of the function vanishes. Conversely, since $\delta v_{\text{ext}} = \chi^{-1} \delta \rho$ the physically meaningful space, from charge conservation, on which χ^{-1} or, equivalently, $-\delta^2 F / \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')$ should operate, is also spanned by functions of the form $\int \delta \rho(\mathbf{r}) d\mathbf{r} = 0$. The equivalence of χ^{-1} and $-\delta^2 F / \delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')$ is thus consistent and physically meaningful in this restricted subspace.

Stability requirements place restrictions on the values of the eigenvalues χ^{-1} [4, 6]. For an arbitrary internal charge fluctuation, since at equilibrium stability it is required that $\delta \rho = 0$, the change in E_{el} must be positive, and to second order in $\delta \rho$ this is given by

$$\Delta E_{\text{el}} = -\frac{1}{2} \iint \delta \rho(\mathbf{r}) \chi^{-1}(\mathbf{r}, \mathbf{r}') \delta \rho(\mathbf{r}') d\mathbf{r} d\mathbf{r}'. \quad (14)$$

Thus χ^{-1} is a non-positive-definite operator in the subspace where it is defined, and the eigenvalues of χ^{-1} must hence all be negative; $\chi_n^{-1} < 0$.

If we expand $F[\rho]$ we can write χ^{-1} as

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{\delta^2 T}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} - \frac{\delta v_{\text{sc}}(\mathbf{r})}{\delta \rho(\mathbf{r}')}. \quad (15)$$

The self-consistent potential is usually expressed in some manageable form, but the functional dependence of $T[\rho]$ on the charge density, unfortunately, is only known in a few limiting cases (see section 3).

When we apply the Hellmann-Feynman theorem [8] to the ground-state energy $E_g[\rho]$ of the independent-particle Hamiltonian

$$E_g[\rho] = T[\rho] + \int v_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} \quad (16)$$

we have

$$\frac{\delta E_g}{\delta \rho(\mathbf{r})} = \int \rho(\mathbf{r}') \frac{\delta v_{\text{eff}}(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' = \frac{\delta T}{\delta \rho(\mathbf{r})} + \int \rho(\mathbf{r}') \frac{\delta v_{\text{eff}}(\mathbf{r}')}{\delta \rho(\mathbf{r})} d\mathbf{r}' + v_{\text{eff}}(\mathbf{r})$$

hence

$$\frac{\delta T}{\delta \rho(\mathbf{r})} = -v_{\text{eff}}(\mathbf{r}) + \text{constant.} \quad (17)$$

We define the inverse of the independent-particle polarizability, χ_0^{-1} , as

$$\chi_0^{-1}(\mathbf{r}, \mathbf{r}') = -\frac{\delta T}{\delta \rho(\mathbf{r}) \delta \rho(\mathbf{r}')} = \frac{\delta v_{\text{eff}}(\mathbf{r})}{\delta \rho(\mathbf{r}')}. \quad (18)$$

The inverse polarizability for the system can thus be expressed as

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') = \chi_0^{-1}(\mathbf{r}, \mathbf{r}') - \frac{\delta v_{\text{sc}}(\mathbf{r})}{\delta \rho(\mathbf{r}')} \quad (19)$$

or in a more compact form

$$\chi = \left[\mathbf{1} - \chi_0 \frac{\delta v_{\text{sc}}}{\delta \rho} \right]^{-1} \chi_0 \quad (20)$$

where $\mathbf{1}$ is the unit matrix. For a given v_{sc} the external potential v_{ext} is a unique functional of ρ and this dependence has to be taken into account when the functional derivative of v_{eff} is taken. From (18) it is evident that the independent-particle polarizability χ_0^{-1} relates a fluctuation in the charge density to a change in the effective single-particle potential δv_{eff} , thus

$$\delta v_{\text{eff}} = \chi_0^{-1} \delta \rho, \quad \delta \rho = \chi_0 \delta v_{\text{eff}}. \quad (21)$$

From perturbation theory the standard expression for χ_0 in terms of eigenfunctions and eigenvectors of the independent-particle Hamiltonian is [9]

$$\chi_0(\mathbf{r}, \mathbf{r}') = 2 \sum_{i,j} \frac{n_i - n_j}{\epsilon_i - \epsilon_j} \psi_i(\mathbf{r}) \psi_j^*(\mathbf{r}') \psi_j(\mathbf{r}) \psi_i^*(\mathbf{r}') \quad (22)$$

where the factor two comes from spin degeneracy and the n_i are occupation factors. This expression involves an infinite summation over products of occupied and empty eigenfunctions, and it is in general a demanding task to compute (22) accurately. From (18) it is clear that χ_0 is a functional of the ground-state charge density. In the following sections it will be shown that χ_0 and hence χ can be expressed in terms of the occupied wavefunctions only.

3. Polarizability for the hydrogen atom

In the case of hydrogen we consider a single electron moving in the potential of a proton, and in the non-relativistic treatment the energy functional F involves only the kinetic energy (i.e. we do not treat it in the density functional formalism). The ground-state wavefunction is non-degenerate and hence it is a real function. The charge density is given by

$$\rho(\mathbf{r}) = \psi_0(\mathbf{r})\psi_0(\mathbf{r}) \quad (23)$$

where $\psi_0(\mathbf{r})$ is the ground-state wavefunction. The kinetic energy becomes

$$\begin{aligned} T[\rho] &= \int \left[-\frac{1}{2}\psi_0(\mathbf{r})\nabla^2\psi_0(\mathbf{r}) \right] d\mathbf{r} = \int \frac{1}{2}\nabla\psi_0(\mathbf{r}) \cdot \nabla\psi_0(\mathbf{r}) d\mathbf{r} \\ &= \int \frac{\nabla\rho(\mathbf{r}) \cdot \nabla\rho(\mathbf{r})}{8\rho(\mathbf{r})} d\mathbf{r}. \end{aligned} \quad (24)$$

Equation (24) gives an explicit expression for the kinetic energy as a functional of the ground-state charge density. From (15), since $F \equiv T$, we now have for the inverse of the polarizability

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') = \frac{1}{4} \left[\frac{\nabla\rho(\mathbf{r}) \cdot \nabla\rho(\mathbf{r})}{\rho(\mathbf{r})^3} - \frac{\nabla\rho(\mathbf{r}) \cdot \nabla}{\rho(\mathbf{r})^2} - \frac{\nabla^2\rho(\mathbf{r})}{\rho(\mathbf{r})^2} + \frac{\nabla^2}{\rho(\mathbf{r})} \right] \delta(\mathbf{r} - \mathbf{r}'). \quad (25)$$

To our knowledge this is the only known expression of the inverse for the polarizability of a system in terms of the ground-state charge density. It is a simple matter to show that this is indeed the inverse in the subspace discussed in section 2. If we substitute for $\delta(\mathbf{r} - \mathbf{r}')$ by $\psi_0(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')/\psi_0(\mathbf{r})$, and expand $\delta(\mathbf{r} - \mathbf{r}')$ in terms of the eigenvectors of H , we can rewrite equation (25) as

$$\chi^{-1}(\mathbf{r}, \mathbf{r}') = \frac{1}{2\psi_0(\mathbf{r})} \left[\sum_j (\epsilon_0 - \epsilon_j) \psi_j(\mathbf{r})\psi_j(\mathbf{r}') \right] \frac{1}{\psi_0(\mathbf{r}')} \quad (26)$$

where we have chosen the eigenfunctions to be real. The polarizability can be written as

$$\chi(\mathbf{r}, \mathbf{r}') = 2 \sum_{j \neq 0} \frac{1}{\epsilon_0 - \epsilon_j} \psi_0(\mathbf{r})\psi_j(\mathbf{r})\psi_j(\mathbf{r}')\psi_0(\mathbf{r}'). \quad (27)$$

From (26) and (27) we have

$$\int \chi^{-1}(\mathbf{r}, \mathbf{r}_1)\chi(\mathbf{r}_1, \mathbf{r}') = \frac{1}{\psi_0(\mathbf{r})} \left[\sum_{j \neq 0} \psi_j(\mathbf{r})\psi_j(\mathbf{r}') \right] \psi_0(\mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') - \rho(\mathbf{r}'). \quad (28)$$

The charge density $\rho(\mathbf{r})$ is exactly the null vector of χ^{-1} , as can be seen by operating on $\rho(\mathbf{r})$ using (26). Furthermore, $\int \rho(\mathbf{r})d\mathbf{r} = 1$, and hence is not an element of the subspace discussed in section 2. Thus, if we project out the null space of χ^{-1} , the inverse of χ exists and is given by (25) or (26).

4. Polarizability in terms of occupied wavefunctions

In this section we choose the eigenfunctions ψ_i of our single-particle Hamiltonian to be real. We define the function $t_i(\mathbf{r}, \mathbf{r}')$ by

$$t_i^{-1}(\mathbf{r}, \mathbf{r}') = \sum_{j \neq i} \frac{\psi_i(\mathbf{r})\psi_j(\mathbf{r})\psi_j(\mathbf{r}')\psi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j}. \quad (29)$$

Summing over all occupied states we have

$$\begin{aligned} 4 \sum_i^{\text{occ}} t_i^{-1}(\mathbf{r}, \mathbf{r}') &= 4 \sum_i^{\text{occ}} \sum_{j \neq i} \frac{\psi_i(\mathbf{r})\psi_j(\mathbf{r})\psi_j(\mathbf{r}')\psi_i(\mathbf{r}')}{\epsilon_i - \epsilon_j} \\ &= 2 \sum_{i,j} \frac{n_i - n_j}{\epsilon_i - \epsilon_j} \psi_i(\mathbf{r})\psi_j^*(\mathbf{r}')\psi_j(\mathbf{r})\psi_i^*(\mathbf{r}') \\ &= \chi_0(\mathbf{r}, \mathbf{r}'). \end{aligned} \quad (30)$$

Consider the expression

$$t_i(\mathbf{r}, \mathbf{r}') = \frac{1}{2} \left[\frac{2\nabla\psi_i(\mathbf{r}) \cdot \nabla\psi_i(\mathbf{r})}{\psi_i(\mathbf{r})^4} - \frac{2\nabla\psi_i(\mathbf{r}) \cdot \nabla}{\psi_i(\mathbf{r})^3} - \frac{2\nabla^2\psi_i(\mathbf{r})}{\psi_i(\mathbf{r})^3} + \frac{\nabla^2}{\psi_i(\mathbf{r})^2} \right] \delta(\mathbf{r} - \mathbf{r}'). \quad (31)$$

In an analogous way to the derivation of (28) we find that

$$\int t_i(\mathbf{r}, \mathbf{r}_1) t_i^{-1}(\mathbf{r}_1, \mathbf{r}') d\mathbf{r}_1 = \delta(\mathbf{r} - \mathbf{r}') - \psi_i(\mathbf{r}')^2. \quad (32)$$

Now $\psi_i(\mathbf{r})^2$ is a null vector of $t_i(\mathbf{r}, \mathbf{r}')$. This can easily be proved by rewriting (31) as

$$\frac{1}{\psi_i(\mathbf{r})} \left[\sum_j (\epsilon_i - \epsilon_j) \psi_j(\mathbf{r})\psi_j(\mathbf{r}') \right] \frac{1}{\psi_i(\mathbf{r}')} \quad (33)$$

and then operating on $t_i(\mathbf{r}, \mathbf{r}')$ with this expression. The inverse of $t_i(\mathbf{r}, \mathbf{r}')$ will only make sense in the subspace from which this vector has been projected, but since $\int \psi_i(\mathbf{r})^2 d\mathbf{r} \neq 0$ this is consistent with the subspace in which χ^{-1} exists. The inverse $t_i(\mathbf{r}, \mathbf{r}')$ is thus well defined in the subspace in which χ^{-1} is defined. Projecting out the $t_i(\mathbf{r}, \mathbf{r}')$ also makes sense when one considers that, from second-order perturbation theory, the charge fluctuation $\delta\rho$ caused by a perturbation in the external potential does not contain a term proportional to $\psi_i(\mathbf{r})^2$.

From (29), (30) and (31) it follows that we can write

$$\begin{aligned} \chi_0(\mathbf{r}, \mathbf{r}') &= 8 \sum_i^{\text{occ}} \left\{ \left[\frac{2\nabla\psi_i(\mathbf{r}) \cdot \nabla\psi_i(\mathbf{r})}{\psi_i(\mathbf{r})^4} - \frac{2\nabla\psi_i(\mathbf{r}) \cdot \nabla}{\psi_i(\mathbf{r})^3} - \frac{2\nabla^2\psi_i(\mathbf{r})}{\psi_i(\mathbf{r})^3} \right. \right. \\ &\quad \left. \left. + \frac{\nabla^2}{\psi_i(\mathbf{r})^2} \right] \delta(\mathbf{r} - \mathbf{r}') \right\}^{-1} \end{aligned} \quad (34)$$

and from (20) we then have that

$$\chi = \left[1 - \chi_0 \frac{\delta v_{sc}}{\delta \rho} \right]^{-1} \chi_0. \quad (35)$$

Since v_{sc} is a functional of the ground-state charge density (35), with χ_0 given by (34) is an expression for the static polarizability in terms of the occupied wavefunctions of the single particle Hamiltonian. Equation (35) is independent of the approximations used to calculate the eigenfunctions. Exchange-correlation effects are included to the extent that they are taken into account in the approximations used for v_{sc} in the single-particle Hamiltonian. The polarizability, as represented in (35), will be exact if the single-particle potential v_{sc} is exact. A further discussion and an application of (35) can be found in [10].

5. Concluding remarks

In section 2 the dependence of the static polarizability on the ground-state charge density was examined. It was shown that the inverse of the polarizability matrix exists and has a physically meaningful interpretation in a subspace spanned by functions of the form $\int \delta \rho(\mathbf{r}) d\mathbf{r} = 0$. An expression for the polarizability of the hydrogen atom in terms of the ground-state charge density was derived in section 3. Equation (35) expresses the static polarizability in terms of the occupied single-particle states of a single-particle Hamiltonian. This expression is exact within DFT. An application of (35) to a molecular system is in preparation.

Incidentally, equation (24) shows that the kinetic energy density of the hydrogen atom is given by $T[\mathbf{r}, \rho] = \nabla \rho(\mathbf{r}) \cdot \nabla \rho(\mathbf{r}) / 8\rho(\mathbf{r})$. In the semiphenomenological Thomas–Fermi approach, the leading term of the kinetic energy density is taken to be proportional to $\rho^{5/3}$, which is correct for the homogeneous electron gas. This, however, bears no resemblance to (24) and it is therefore not surprising that the Thomas–Fermi approach is not very successful in describing atomic properties [11]. The expressions for the free electron gas and the hydrogen atom must, however, be limiting cases of the same functional that describes the kinetic energy density of an independent system of electrons of density ρ .

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