

Analysis of the linear response function along the adiabatic connection from the Kohn–Sham to the correlated system

Andreas Savin,^{a)} François Colonna, and Marcel Allavena

Laboratoire de Chimie Théorique (CNRS), Université Pierre et Marie Curie 4, Place Jussieu,
F-75252 Paris, France

(Received 25 June 2001; accepted 1 August 2001)

Careful calculations are performed to obtain the radial density–density response function for the He and the Be series. This is also done along the adiabatic connection of the density functional theory (as the system evolves from the real, physical system to the Kohn–Sham one). In this process the electron density is kept constant, while the strength of the interaction between electrons changes. The response functions are analyzed in terms of their eigenvalues and eigenfunctions. The latter change only little along this process. The absolute value of the eigenvalues is in general reduced by the interaction: A screening effect is present. For the near-degenerate systems, we notice that the opposite effect can appear (antiscreeing). © 2001 American Institute of Physics.
[DOI: 10.1063/1.1405011]

I. INTRODUCTION

The Hohenberg–Kohn theorem¹ establishes the mapping between the external potential of a given system, v_{ext} , and the ground state density n . As a chemical process implies a change in v_{ext} it seems natural in this context, as a first step, to study the relationship between small changes in v_{ext} , δv_{ext} , and the corresponding changes in n , δn . The connection between these quantities is given by the linear response function $\chi(\mathbf{r}, \mathbf{r}')$:

$$\delta n(\mathbf{r}) = \int \chi(\mathbf{r}, \mathbf{r}') \delta v_{\text{ext}}(\mathbf{r}') d^3 \mathbf{r}', \quad (1)$$

where $\chi(\mathbf{r}, \mathbf{r}')$ is defined perturbationally. We use a compact notation by introducing the star symbol ($\star$):

$$\delta n = \chi \star \delta v_{\text{ext}}.$$

The aim of this study is to provide more information about χ by performing reasonably accurate calculations for small systems: the He series and the Be series.

The second important aspect of density functional theory (DFT) is the Kohn–Sham approach:² The vast majority of practical calculations are performed by considering the fictitious system of noninteracting electrons, yielding the same density as the (physical) system of interest. As the Hohenberg–Kohn theorem is valid for any type of interaction between particles, there also is a mapping between n and the potential in the Kohn–Sham system, v_{KS} . It is thus interesting to study the corresponding Kohn–Sham response function χ_{KS} :

$$\delta n = \chi_{\text{KS}} \star \delta v_{\text{KS}}.$$

It is usually assumed that it is possible to reach the Kohn–Sham system by switching off the electron–electron interaction ($1/r_{12} \rightarrow \lambda/r_{12}$; $0 \leq \lambda \leq 1$). This adiabatic connection plays a central role in DFT, being the bridge between the

physical and Kohn–Sham systems; it is the way most approximations are understood. Although it is not necessary (cf. Refs. 3–6), it is usually preferred to keep the density constant along the adiabatic connection.^{7–11} In order to achieve it, the external potential changes continuously from v_{ext} to v_{KS} : $v_{\text{ext}} \rightarrow v_{\lambda}$ ($v_{\lambda=1} = v_{\text{ext}}$, $v_{\lambda=0} = v_{\text{KS}}$). We will also show in the following some results for the linear response function along the adiabatic connection $\chi(\lambda) = \chi(\mathbf{r}, \mathbf{r}'; \lambda)$:

$$\delta n = \chi(\lambda) \star \delta v_{\lambda}.$$

Usually, approximations are made only for the exchange–correlation part of the energy, which corresponds to approximating the exchange–correlation potential, v_{xc} :

$$v_{\text{KS}} = v_{\text{ext}} + v_h + v_{\text{xc}},$$

where $v_h = \int (n/r_{12}) d^3 r_2$. Now using the fact that the same density change is obtained by δv_{KS} and δv_{ext} , and after introducing the inverse response functions (see, e.g., Ref. 12), χ^{-1} , χ_{KS}^{-1} ,

$$\delta v_{\text{ext}} = \chi^{-1} \star \delta n,$$

one obtains

$$\chi_{\text{KS}}^{-1} = \chi^{-1} + \frac{1}{r_{12}} + f_{\text{xc}},$$

where $f_{\text{xc}} = \delta v_{\text{xc}} / \delta n$. Thus the problem of finding χ or (χ^{-1}) is transferred, in the Kohn–Sham approach, to that of finding f_{xc} .

In the simplest approach, the random phase approximation (RPA), f_{xc} is set to zero:

$$\chi_{\text{RPA}}^{-1} = \chi_{\text{KS}}^{-1} - \frac{1}{r_{12}}.$$

Please note that χ_{RPA} contains a self-interaction error, as for any one-electron system, χ is equal to χ_{KS} and not to χ_{RPA} . This error is also present in the popular local density approximation, where $v_{\text{xc}}(\mathbf{r})$ is a function of $n(\mathbf{r})$, and

^{a)}Electronic mail: savin@lct.jussieu.fr

$f_{xc}(\mathbf{r}, \mathbf{r}') = \delta v_{xc}(\mathbf{r}) / \delta n(\mathbf{r}')$ thus has the form $f_{xc}(n(\mathbf{r})) \delta(\mathbf{r} - \mathbf{r}')$. Of course, this is also wrong, as for a one-electron system $f_{xc}(\mathbf{r}, \mathbf{r}') = -1/|\mathbf{r} - \mathbf{r}'|$.

The connection between δv_{ext} and δv_{KS} is given by

$$\delta v_{KS} = \epsilon^{-1} \star \delta v_{ext},$$

where ϵ^{-1} is the inverse dielectric function, which can be written as

$$\epsilon^{-1} = \chi_{KS}^{-1} \star \chi. \quad (2)$$

Physically, ϵ^{-1} reflects the effect of the interaction between electrons, and one might expect that this produces a screening of δv_{ext} and thus a reduction of χ with respect to χ_{KS} ($\epsilon^{-1} < 1$). One of the objectives of this work is to check whether this is true in the systems considered.

With $\chi(\lambda)$ one has to deal with functions of six variables. As we are interested in δv in atoms, we develop these functions in terms of spherical harmonics,

$$\begin{aligned} \chi(\mathbf{r}, \mathbf{r}'; \lambda) = & \sum_{l,m} \sum_{l',m'} \chi(r, l, m; r', l', m'; \lambda) \\ & \times Y_{lm}(\Omega) Y_{l'm'}(\Omega'). \end{aligned}$$

As we consider only spherical densities $\delta n(\mathbf{r}) = \delta n(r)$, and furthermore only spherical potentials $\delta v(\mathbf{r}) = \delta v(r)$. Thus,

$$\begin{aligned} \delta n(r) = & \int \chi(r, l=0, m=0; r', l'=0, m'=0) \\ & \times \delta v_{ext}(r') r'^2 dr'. \end{aligned}$$

To simplify notation, we will drop in what follows $l=l'=m=m'=0$, and write

$$\chi_r(r, r'; \lambda) = \frac{1}{4\pi} \chi(r, l=0, m=0; r', l'=0, m'=0; \lambda). \quad (3)$$

In order to manipulate the information we will consider the eigenvector decomposition, see, e.g., Ref. 13:

$$\chi_r(r, r'; g l) = \sum_i \kappa_i(\lambda) \psi_i(r; \lambda) \psi_i(r'; \lambda),$$

where the ψ_i are orthonormal:

$$4\pi \int r^2 \psi_i(r; \lambda) \psi_j(r; \lambda) dr = \delta_{ij}.$$

One advantage of this decomposition is that we can get the best approximation to χ_r (in a least-squares sense) by cutting off the above-mentioned expansion by selection of the terms corresponding to the most important eigenvalues. Notice that a change of the potential by a constant does not modify the density, implying $\int \chi = 0$; this in turn means that

$$4\pi \int r^2 \psi_i(r) dr = 0$$

so that the $\psi_i(r)$ necessarily have nodes.

II. METHOD

The response functions are derived from perturbation theory, by using

$$\delta n(\mathbf{r}) = 2 \langle \Psi^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi^{(1)} \rangle,$$

where $\Psi^{(0)}$ is the unperturbed ground state wave function, $\Psi^{(1)}$ the first-order correction to it, due to the perturbing potential $\delta v(\mathbf{r}')$, and $\hat{\rho}(\mathbf{r})$ the density operator. To obtain $\chi_r(r, r')$ we use Eqs. (1) and (3):

$$\delta n(\mathbf{r}) = \delta n(r) = \int \chi_r(r, \tilde{r}) \delta v(\tilde{r}) 4\pi \tilde{r}^2 d\tilde{r}. \quad (4)$$

Thus, $\chi_r(r, r')$ is $\delta n(r)$ obtained with $\delta v(\tilde{r}) = \delta(\tilde{r} - r')/4\pi \tilde{r}^2$. In some cases, such as the hydrogen atom, $\Psi^{(1)}$ and thus χ_r can be obtained analytically. In many cases, like the noninteracting systems, it is common to use the sum-over-states formula to obtain $\Psi^{(1)}$ and thus χ_r . With many programs, it is also convenient to use a small finite perturbing potential and analyze the resulting density.

For the noninteracting closed-shell system, it is easy to use the expression of χ_{KS} in terms of Kohn–Sham orbitals, φ_i , and eigenvalues ϵ_i (in a finite basis):

$$\chi_{KS}(\mathbf{r}, \mathbf{r}') = 4 \sum_i^{\text{occ}} \sum_a^{\text{unocc}} \frac{\varphi_i(\mathbf{r}) \varphi_a(\mathbf{r}) \varphi_i(\mathbf{r}') \varphi_a(\mathbf{r}')}{\epsilon_i - \epsilon_a}. \quad (5)$$

For interacting systems we generate $\chi_r(\lambda)$ in the basis of the $\psi_i(r; \lambda=0)$. To obtain it, we made a configuration interaction calculation after changing the external potential by $\delta v_k(r) = 10^{-3} \psi_k(r, \lambda=0)$, and decompose the resulting density changes onto the same basis $\psi_k(r, \lambda=0)$; from

$$\begin{aligned} \chi_r(r, r'; \lambda) = & \sum_{ij} \chi_{ij}(\lambda) \psi_i(r; \lambda=0) \psi_j(r'; \lambda=0), \\ \delta n^k(r; \lambda) = & \sum_i \delta n_i^k(\lambda) \psi_i(r; \lambda=0), \end{aligned} \quad (6)$$

we obtain that the change in $\delta n_i^k(\lambda) = \int r^2 \delta n^k(r; \lambda) \psi_i(r; \lambda=0) dr$ induced by δv_k will be, to linear order, $10^{-3} \chi_{ik}(\lambda)$. Some technical details are given in Appendices A and B.

We now check some limits of the procedures just described. A first one is given by the finite size of the basis set. One possibility to check it, is to compare the eigenvalues $\kappa_i(\lambda=0)$, for a given basis set, with those obtained from a larger basis set, or those obtained on a dense numerical grid, by using the exact response function of the hydrogen atom (cf. Appendix C). We show in Fig. 1 the decimal logarithm of the first 35 eigenvalues $\kappa_i(\lambda=0)$ of χ_{KS} of the H atom: from calculations on a grid with 256 points and on two Gaussian basis sets. Of course, an increase of the size of the basis set produces a larger domain of validity of the κ_i 's. Figure 1 shows a significant loss of quality of the smaller eigenvalues (notice the logarithmic scale of the plot). It is clear that only a limited number of nodes can be represented with finite basis sets. It is thus not surprising that not all eigenvalues are pertinent. Notice also that χ_r has a number of eigenvalues larger than the number of basis functions. In

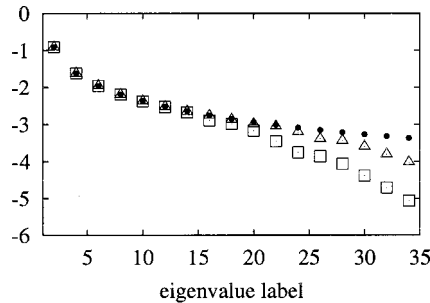


FIG. 1. Decimal logarithm of the 35 first eigenvalues of the hydrogen atom response function. The results obtained on a dense numerical grid are shown as dots, while calculations with 31 and 21 Gaussian s functions are shown as triangles and squares, respectively.

fact, the problem of not describing the small eigenvalues is related to that of linear dependencies in the products of basis functions (see e.g., Refs. 14–16).

The second problem is the finite perturbation approach which was used to obtain $\chi(\lambda \neq 0)$. For $\chi(\lambda = 0)$ the exact δn_i^k are equal to zero for $i \neq k$. Due to the finite perturbation, these δn_i^k are, however, of the order of $(\delta v_k)^2$. For example, for the hydrogen atom, using $\delta v_1(r) = 10^{-3}\psi_1(r)$, the δn_1^1 are of the order of 10^{-4} while the $\delta n_i^1 (i \neq 1)$ are of the order of 10^{-8} or smaller.

III. RESULTS

Typical plots of $r^2\chi(r,r')r'^2$ are shown in Fig. 2, taking as examples the hydrogen, helium, and beryllium atoms. The plot for the H atom shows that there are essentially two regions in the atom (the inner sphere, and the outer shell): A repulsive potential change δv in one of the regions produces a displacement of the radial density from it to the other region. Of course, the opposite effect appears for an attractive δv . The plot for the He atom is similar (cf. Fig. 2). For the Be atom, however, a duplication appears, which we attribute to the shell structure. Such plots can be made for all λ . As the figures look similar, we show only $\lambda = 0$.

We will continue now with the analysis of the eigenvalues, $\kappa_i(\lambda)$, and eigenfunctions, $\psi_i(\lambda)$, of the $\chi_r(\lambda)$. The eigenvalues are given for $\lambda = 0$ and $\lambda = 1$ in Tables I and II. Ordering the eigenfunctions with increasing eigenvalues (the

TABLE I. First seven eigenvalues of the response function in the He series. For each system, $\kappa_i(\lambda=0)$, $\kappa_i(\lambda=1)$, and their ratio $\tilde{\epsilon}_i^{-1} = \kappa_i(\lambda=1)/\kappa_i(\lambda=0)$ are shown (first, second, and third lines, respectively).

	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$	$i=7$
He	-0.51	-0.09	-0.04	-0.02	-0.01	-0.01	-0.01
	-0.40	-0.08	-0.04	-0.02	-0.01	-0.01	-0.01
	0.79	0.97	1.00	1.00	1.00	1.00	1.00
Li ⁺	-0.74	-0.13	-0.06	-0.04	-0.02	-0.02	-0.01
	-0.65	-0.13	-0.06	-0.04	-0.02	-0.02	-0.01
	0.87	0.98	1.00	1.00	1.00	1.00	1.00
Be ⁺²	-0.99	-0.18	-0.08	-0.05	-0.03	-0.02	-0.01
	-0.89	-0.18	-0.08	-0.05	-0.03	-0.02	-0.01
	0.90	0.99	1.00	1.00	1.00	1.00	1.00
B ⁺³	-1.23	-0.23	-0.11	-0.06	-0.04	-0.03	-0.02
	-1.14	-0.23	-0.10	-0.06	-0.04	-0.03	-0.02
	0.92	0.99	1.00	1.00	1.00	1.00	1.00
C ⁺⁴	-1.48	-0.28	-0.13	-0.07	-0.05	-0.03	-0.02
	-1.39	-0.28	-0.13	-0.07	-0.05	-0.03	-0.02
	0.94	0.99	1.00	1.00	1.00	1.00	1.00
N ⁺⁵	-1.72	-0.33	-0.15	-0.09	-0.06	-0.04	-0.03
	-1.63	-0.32	-0.15	-0.09	-0.06	-0.04	-0.03
	0.95	0.99	1.00	1.00	1.00	1.00	1.00
O ⁺⁶	-1.97	-0.37	-0.17	-0.10	-0.06	-0.05	-0.03
	-1.88	-0.37	-0.17	-0.10	-0.06	-0.05	-0.03
	0.95	0.99	1.00	1.00	1.00	1.00	1.00
F ⁺⁷	-2.22	-0.42	-0.19	-0.11	-0.07	-0.05	-0.04
	-2.13	-0.42	-0.19	-0.11	-0.07	-0.05	-0.04
	0.96	0.99	1.00	1.00	1.00	1.00	1.00
Ne ⁺⁸	-2.46	-0.47	-0.22	-0.12	-0.08	-0.06	-0.04
	-2.37	-0.47	-0.21	-0.12	-0.08	-0.06	-0.04
	0.96	0.99	1.00	1.00	1.00	1.00	1.00

eigenvalues are negative, see, e.g., Ref. 17) we observe that in the Be series the first four eigenfunctions are localized in the core region, while the fifth is localized in the valence region (cf. Fig. 3 for Be at $\lambda = 0$). It turns out that the eigenfunctions change only little with λ ; we notice a significant change in the eigenvalues, especially for the first one in each shell. We show in Figs. 4 and 5 the ratio $\kappa_i(\lambda)/\kappa_i(\lambda = 0)$ for the helium and the beryllium atoms. We can also decompose

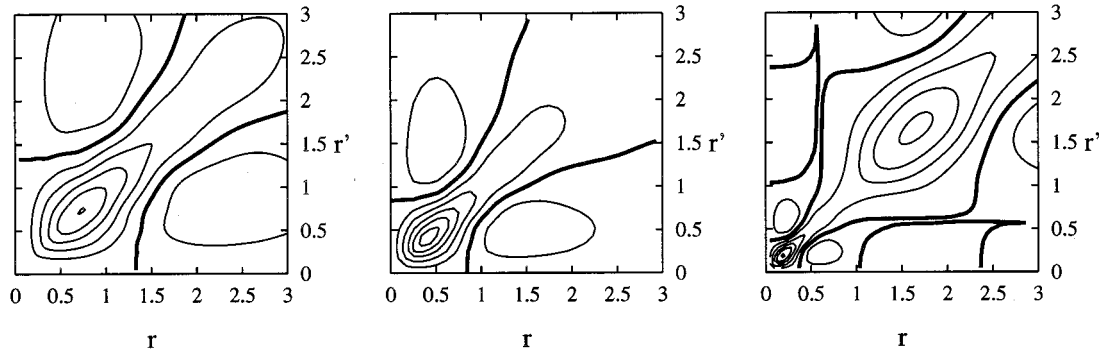


FIG. 2. Isocontour plot of $r^2 r'^2 \chi_r(r, r'; \lambda = 0)$ for the H, He, and Be atoms, from left to right, respectively. The zero contour has been emphasized; $\chi_r(r, r' = r; \lambda = 0) < 0$.

TABLE II. First seven eigenvalues of the response function in the Be series. For each system, $\kappa_i(\lambda=0)$, $\kappa_i(\lambda=1)$, and their ratio $\tilde{\epsilon}_i^{-1} = \kappa_i(\lambda=1)/\kappa_i(\lambda=0)$ are shown (first, second, and third lines, respectively).

	$i=1$	$i=2$	$i=3$	$i=4$	$i=5$	$i=6$	$i=7$
Be	-1.01	-0.18	-0.08	-0.05	-0.04	-0.03	-0.02
	-0.90	-0.18	-0.08	-0.05	-0.04	-0.03	-0.02
	0.90	0.98	1.00	1.00	0.88	1.00	1.00
B^{+1}	-1.26	-0.23	-0.11	-0.06	-0.05	-0.04	-0.03
	-1.16	-0.23	-0.11	-0.06	-0.05	-0.04	-0.03
	0.92	0.99	1.00	1.00	0.95	1.00	1.00
C^{+2}	-1.52	-0.28	-0.13	-0.07	-0.06	-0.05	-0.03
	-1.42	-0.28	-0.13	-0.07	-0.06	-0.05	-0.03
	0.93	0.99	1.00	1.00	0.98	1.00	1.00
N^{+3}	-1.78	-0.33	-0.15	-0.09	-0.07	-0.06	-0.04
	-1.68	-0.33	-0.15	-0.09	-0.07	-0.06	-0.04
	0.95	0.99	1.00	1.00	1.01	1.00	1.00
O^{+4}	-2.03	-0.38	-0.17	-0.10	-0.08	-0.07	-0.05
	-1.94	-0.38	-0.17	-0.10	-0.09	-0.07	-0.05
	0.96	1.00	1.00	1.00	1.04	1.00	1.01
F^{+5}	-2.29	-0.43	-0.20	-0.11	-0.09	-0.07	-0.05
	-2.21	-0.43	-0.20	-0.11	-0.10	-0.08	-0.05
	0.96	1.00	1.00	1.00	1.07	1.00	1.01
Ne^{+6}	-2.55	-0.48	-0.22	-0.13	-0.11	-0.08	-0.06
	-2.47	-0.48	-0.22	-0.13	-0.12	-0.08	-0.06
	0.97	1.00	1.00	1.00	1.09	1.00	1.01

$\chi_r(\lambda)$ on the basis of the eigenfunctions of $\chi_r(\lambda=0)$, $\psi_i(\lambda=0)$, as in Eq. (6). Within our accuracy, χ_{ij} is a nearly diagonal matrix, as can be seen in Fig. 6. This in turn means that ϵ^{-1} [Eq. (2)] will also be nearly diagonal in this basis:

$$\begin{aligned}\epsilon^{-1}(r, r'; \lambda) &= \sum_{ij} \epsilon_{ij}^{-1}(\lambda) \psi_i(r; \lambda=0) \psi_j(r'; \lambda=0) \\ &\approx \sum_i \tilde{\epsilon}_i^{-1}(\lambda) \psi_i(r; \lambda=0) \psi_i(r'; \lambda=0),\end{aligned}$$

where $\tilde{\epsilon}_i^{-1}(\lambda) = \kappa_i(\lambda)/\kappa_i(\lambda=0)$. For example, for the beryl-

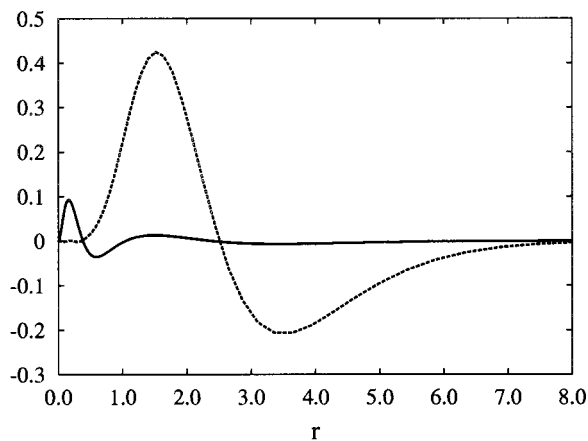


FIG. 3. First and fifth eigenvectors of χ_{KS} for the Be atom: $r^2 \psi_1(r; \lambda=0)$ (continuous line) and $r^2 \psi_5(r; \lambda=0)$ (dotted line).

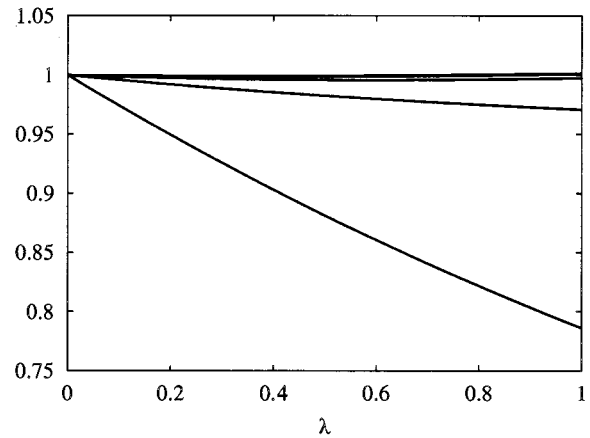


FIG. 4. Dependence of the first few eigenvalues of the inverse dielectric function, approximated by the ratio of the eigenvalues of $\chi^\lambda: \tilde{\epsilon}_i^{-1} = \kappa_i(\lambda)/\kappa_i(\lambda=0)$ on the adiabatic coupling constant λ . The lowest curve corresponds to $i=1$; for the He atom.

lium atom, we have for $i=5$ (the most important valence eigenstate) $\tilde{\epsilon}_5^{-1}(\lambda=1)=0.884$ within 0.5% of $\epsilon_{55}^{-1}(\lambda=1)=0.888$.

We now turn to the question of screening. We will speak about “screening” when $\tilde{\epsilon}_i^{-1} < 1$, and about “antiscreeing” when $\tilde{\epsilon}_i^{-1} > 1$. Some $\tilde{\epsilon}_i^{-1}$ were already shown in Figs. 4 and 5. We see that in these cases screening is present. We now show in Fig. 7 the plot of $\tilde{\epsilon}^{-1}(\lambda)$ for Ne^{6+} . It turns out that $\tilde{\epsilon}_5^{-1}$ significantly increases with λ . Thus, for the valence shell of Ne^{6+} antiscreeing appears. This change appears for N^{3+} in the Be series, as can be seen in Fig. 8, where $\tilde{\epsilon}_5^{-1}(\lambda=1)$ is shown as a function of nuclear charge of the ion, Z . We could not detect, however, antiscreeing effects at RPA level. We thus attribute antiscreeing to the increase in $\kappa_i(\lambda)/\kappa_i(\lambda=0)$ produced by f_{xc} .

In order to understand the antiscreeing in the Be series, remember that two configurations (Φ_s and Φ_p , corresponding to $1s^2 2s^2$ and $1s^2 2p^2$) are both important. We should

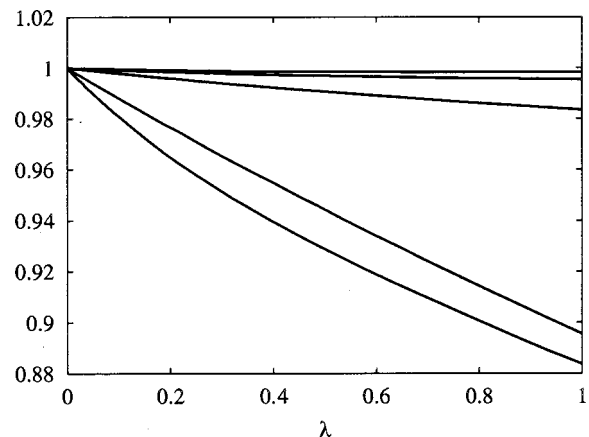


FIG. 5. Dependence of the first few eigenvalues of the inverse dielectric function, approximated by the ratio of the eigenvalues of $\chi^\lambda: \tilde{\epsilon}_i^{-1} = \kappa_i(\lambda)/\kappa_i(\lambda=0)$ on the adiabatic coupling constant λ . From the lowest curve to the uppermost curve, we have $i=5,1,2,3,4$ for the Be atom.

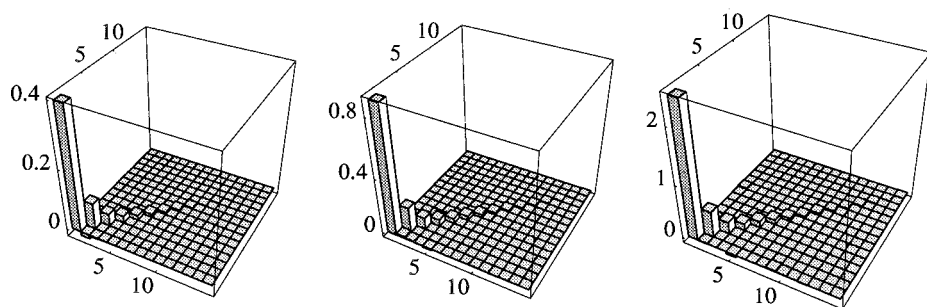


FIG. 6. Plots of the $\chi_{ij}^{\lambda=1}$ matrix elements on the basis of the eigenvectors of $\chi^{\lambda=0}$ for He, Be, and Ne^{6+} (left-hand side, middle, and right-hand side).

thus consider, as a first approximation to the eigenstates (see also Ref. 18):

$$\Psi_0^{(0)} = \cos \alpha \Phi_s - \sin \alpha \Phi_p,$$

$$\Psi_1^{(0)} = \sin \alpha \Phi_s + \cos \alpha \Phi_p.$$

To zeroth order, the response function is

$$\chi^{(0)}(\mathbf{r}, \mathbf{r}') = \frac{\langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_1^{(0)} \rangle \langle \Psi_1^{(0)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(0)} \rangle}{\Delta E_{01}} + \sum_{i \geq 1} \frac{\langle \Psi_0^{(0)} | \hat{\rho}(\mathbf{r}) | \Psi_i^{(0)} \rangle \langle \Psi_i^{(0)} | \hat{\rho}(\mathbf{r}') | \Psi_0^{(0)} \rangle}{\Delta E_{0i}}, \quad (7)$$

where ΔE_{0i} are the energy denominators, and $\Psi_i^{(0)}$ the unperturbed eigenfunctions. The first term on the right-hand side reflects the effect of near degeneracy, while the second is general. As Φ_s and Φ_p differ by two orbitals, and $\hat{\rho}(\mathbf{r})$ is a one-electron operator, $\langle \Phi_s | \hat{\rho}(\mathbf{r}) | \Phi_p \rangle = 0$ and the first term on the right-hand side of Eq. (7) has a numerator:

$$\cos^2 \alpha \sin^2 \alpha (\langle \Phi_p | \hat{\rho}(\mathbf{r}) | \Phi_p \rangle - \langle \Phi_s | \hat{\rho}(\mathbf{r}) | \Phi_s \rangle) \times (\langle \Phi_p | \hat{\rho}(\mathbf{r}') | \Phi_p \rangle - \langle \Phi_s | \hat{\rho}(\mathbf{r}') | \Phi_s \rangle). \quad (8)$$

The second term has contributions of the type

$$\cos^2 \alpha (\langle \Phi_s | \hat{\rho}(\mathbf{r}) | \Phi_v \rangle - \langle \Phi_v | \hat{\rho}(\mathbf{r}) | \Phi_s \rangle), \quad (9)$$

where $\Phi_v \neq \Phi_s$ or Φ_p , or

$$\sin^2 \alpha (\langle \Phi_p | \hat{\rho}(\mathbf{r}) | \Phi_v \rangle - \langle \Phi_v | \hat{\rho}(\mathbf{r}) | \Phi_p \rangle).$$

Φ_v contains monoexcitations from Φ_s or Φ_p ; ($\langle \Phi_s | \hat{\rho}(\mathbf{r}) | \Phi_v \rangle$ and $\langle \Phi_p | \hat{\rho}(\mathbf{r}) | \Phi_v \rangle$ cannot both be nonzero, and we thus do not have terms like $\langle \Phi_s | \hat{\rho}(\mathbf{r}) | \Phi_v \rangle \times \langle \Phi_v | \hat{\rho}(\mathbf{r}) | \Phi_p \rangle$). Thus when $\alpha=0$ only terms of the type Eq. (9) are left. This corresponds to the noninteracting case for the system considered. When α is nonzero these terms, Eq. (9), become smaller than for $\alpha=0$, reducing the response (screening has occurred). Notice, however, that an opposite effect is also present [cf. Eq. (8)]: A contribution to χ arises, which was not present at $\alpha=0$. We attribute to this term, related to near degeneracy, the appearance of antiscreening. The increase of antiscreening with the nuclear charge Z is essentially related to the change of the energy denominator ΔE_{01} with Z .

IV. CONCLUSION AND PERSPECTIVES

In this paper we showed the static linear density–density response function of Kohn–Sham systems having the densities of the He atom, the Be atom, and their isoelectronic ions, up to $Z=10$. Furthermore, we studied the change of the response functions with λ , a constant multiplying the electron–electron interaction operator, while keeping the density constant. It turned out that the eigenstates of the response functions do not significantly change with λ , while their eigenvalues do. There is a significant difference between the He and the Be series, in the change of the eigenvalues with

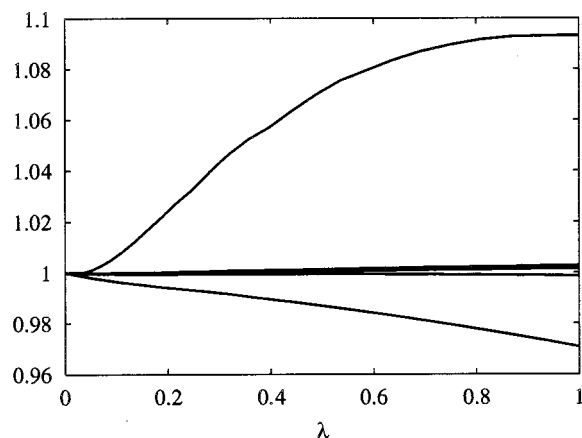


FIG. 7. Dependence of the first few eigenvalues of the inverse dielectric function, approximated by the ratio of the eigenvalues of $\chi^\lambda: \epsilon_i^{-1} = \kappa_i(\lambda)/\kappa_i(\lambda=0)$ on the adiabatic coupling constant λ . The lowest curve corresponds to $i=1$. From the lowest curve to the uppermost curve, we have $i=1,2,3,4,5$ for the Ne^{6+} ion.

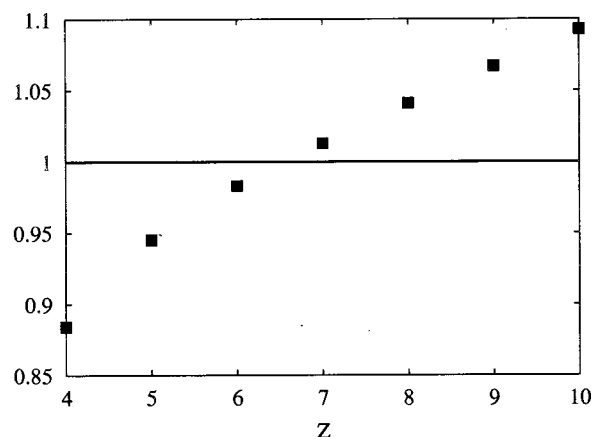


FIG. 8. Z-dependent antiscreening effect of the fifth component of the inverse dielectric function, approximated by the ratio of the eigenvalues of $\chi^\lambda: \epsilon_5^{-1} = \kappa_5(\lambda=1)/\kappa_5(\lambda=0)$ for the Be series.

TABLE III. Central exponents α_c [Eq. (A1)] of the even tempered Gaussian basis sets.

System	s	pdf
He	40.0	3.0
Li ⁺	85.5	7.5
Be ²⁺	350.0	15.0
B ³⁺	475.0	23.0
C ⁴⁺	663.0	34.0
N ⁵⁺	990.0	48.0
O ⁶⁺	1200.0	65.0
F ⁷⁺	1612.0	82.5
Ne ⁸⁺	2030.0	100.0
Be	4.0	1.0
B ⁺	4.6	3.3
C ²⁺	10.0	5.0
N ³⁺	7.5	8.0
O ⁴⁺	12.0	11.0
F ⁵⁺	100.0	9.0
Ne ⁶⁺	130.0	15.0

λ . While electron–electron interaction in general screens the effect of the perturbing potential, we observe the opposite effect for higher Z in the Be series. This effect is connected with the contribution coming from the variation of the exchange–correlation potential with the density, f_{xc} , and gives a further indication about the difficulty to properly describe it (see, e.g., Ref. 19).

It can be hoped that a better knowledge of χ will finally help one to construct better approximations to f_{xc} , and to the exchange–correlation functionals, in a similar way as knowledge of exact Kohn–Sham potentials are useful (see, e.g., Ref. 20).

ACKNOWLEDGMENTS

The authors would like to thank John F. Dobson (Nathan University, Brisbane, Australia), Walter Kohn (University of California at Santa Barbara), and E. Zaremba (Queen's University, Kingston, Canada) for stimulating discussions. We are grateful to the IDRIS (CNRS, Orsay, France) for the allocation of computing time.

APPENDIX A: BASIS SETS

Uncontracted even tempered Gaussian basis sets, up to f functions, were used in the calculations. For each angular quantum number, M exponents α_n were produced by the rule

$$\alpha_n = \alpha_c \delta^{(2n-M-1)/2}, \quad n = 1, \dots, M. \quad (\text{A1})$$

$\delta = 2.1$ for all systems. M has been chosen to be 21 for all the s functions, 7 for the p functions of the helium series, 9 for the p functions of the beryllium series, and 5 and 3 for the d and f functions, respectively. The central exponents α_c are given in Table III. For H (Fig. 1) 21 (with $\delta = 2.1$) and 31 (with $\delta = 1.7$) s -type functions, centered at $\alpha_c = 10$ were used.

APPENDIX B: CALCULATION OF THE RESPONSE FUNCTION χ_{KS} FROM THE EIGENVECTORS OF THE OVERLAP MATRIX PRODUCTS OF PRIMITIVE GAUSSIANS

Given a set of Gaussian primitive functions $g_p(\mathbf{r})$, let $\pi_m = g_p(\mathbf{r})g_q(\mathbf{r})$, where p runs over the primitives appearing in the occupied orbitals and q runs over those appearing in the virtual orbitals; m is a composite index. To avoid problems due to linear dependencies between the π_m , we choose to develop the χ_{KS} function on the eigenvectors $\eta_a(\mathbf{r})$ of the overlap matrix of the π_m , $S_{a,b}^\pi = \langle \pi_a | \pi_b \rangle$,

$$S^\pi \eta_a(\mathbf{r}) = \Delta_a \eta_a(\mathbf{r}),$$

where the Δ_a are the eigenvalues. The Δ_a are sorted and only those eigenvectors corresponding to ($\Delta_a > 10^{-12}$) are used in the following. The orthogonal η are developed on the π functions with

$$\eta_a = \sum_m A_{a,m} \pi_m(\mathbf{r}).$$

In the η basis, using Eq. (5), the matrix representation of $\chi_{KS}(\mathbf{r}, \mathbf{r}')$, χ^η , is given by

$$\begin{aligned} \chi_{KS,ab}^\eta &= \int \int \chi_{KS}(\mathbf{r}, \mathbf{r}') \eta_a(\mathbf{r}) \eta_b(\mathbf{r}') d^3\mathbf{r} d^3\mathbf{r}' \\ &= \sum_i^{\text{occ}} \sum_j^{\text{vir}} \frac{4}{\epsilon_i - \epsilon_j} I_{ija}^\eta I_{ijb}^\eta, \end{aligned}$$

where the overlap integrals I_{ija}^η are given by

$$I_{ija}^\eta = \int \varphi_i(\mathbf{r}) \varphi_j(\mathbf{r}) \eta_a(\mathbf{r}) d^3\mathbf{r}.$$

Diagonalization of χ^η in the η_a basis produces the orthonormal eigenvectors $C_{a,i}$ and the eigenvalues κ_i . They, in turn, give the development of the $\psi_i(\mathbf{r})$ on the primitive Gaussian pairs $\pi_m(\mathbf{r})$:

$$\psi_i(\mathbf{r}) = \sum_a C_{i,a} \eta_a(\mathbf{r}) = \sum_a C_{i,a} \sum_m A_{a,m} \pi_m(\mathbf{r}).$$

As for high i , the numerical values of the λ_i may lose significance (becoming 10^{-16} or lower or even positive), only the first few largest in absolute value ($< 10^{-6}$) are kept (19 for He series and 18 for Be series).

APPENDIX C: EXACT RESPONSE FUNCTION χ_R OF THE HYDROGEN ATOM

In order to facilitate the reading of the present paper we give in the following a derivation of $\chi_r(r, r')$ for the hydrogen atom, although it is given, at least implicitly, in the literature (see, e.g., Ref. 21).

In the case of noninteracting spherically symmetric systems it is customary to replace the radial functions $R(r)$ by $u(r) = rR(r)$, in order to write the Schrödinger equation as that of a particle in one dimension:

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v(r) \right] u(r) = E u(r),$$

where l is the angular momentum quantum number.

When the potential $v(r)$ is decomposed into two parts, $v(r) = v^{(0)}(r) + v^{(1)}(r)$, and the solution for $v^{(0)}(r)$ is supposed to be known ($u^{(0)}$ and $E^{(0)}$), the first-order equation is written as

$$\left[-\frac{1}{2} \frac{d^2}{dr^2} + \frac{l(l+1)}{2r^2} + v(0) - E^{(0)} \right] u^{(1)} + [v^{(1)} - E^{(1)}] u^{(0)} = 0.$$

This will be solved by using a method proposed by Dalgarno and Lewis²² and Young and March.²³ A substitution introduces the function $f(r): u^{(1)} = fu^{(0)}$. Let us take $l=0$ and drop the subscript l . Multiplying the equation by $-2u^{(0)}$ one obtains

$$\frac{d}{dr} \left[(u^{(0)})^2 \frac{df}{dr} \right] = 2(v^{(1)} - E^{(1)})(u^{(0)})^2.$$

If $u^{(0)}$ is nodeless, a first integration yields as $u^{(0)}(r \rightarrow \infty) \rightarrow 0$:

$$\frac{df}{dr} = -\frac{2}{(u^{(0)}(r))^2} \int_r^\infty [v^{(1)}(\tilde{r}) - E^{(1)}] (u^{(0)}(\tilde{r}))^2 d\tilde{r},$$

which can be integrated once more to

$$f(r) = -\int dr \frac{2}{(u^{(0)}(r))^2} \int_r^\infty d\tilde{r} [v^{(1)}(\tilde{r}) - E^{(1)}] \times (u^{(0)}(\tilde{r}))^2 + C. \quad (C1)$$

A change in the potential equal to $\eta[\delta(r-r')]/4\pi r^2$, produces a change in the density having a term linear in η equal to $\eta\chi(r, r')$, cf. Eq. (4), where η is infinitesimal. χ_r is obtained by constructing the first-order change in the density due to $v^{(1)}(r) = [\delta(\tilde{r}-r')]/4\pi r^2$. For this potential, $E^{(1)}$ is given by

$$E^{(1)} = \int \left(R^{(0)}(r) \frac{1}{\sqrt{4\pi}} \right)^2 \frac{\delta(\tilde{r}-r_0)}{4\pi\tilde{r}^2} 4\pi\tilde{r}^2 d\tilde{r}, \\ = \frac{1}{4\pi} (R^{(0)}(r_0))^2$$

where $R^{(0)}(r) = 2e^{-r}$, the radial function of the H atom. Inserting this result into Eq. (C1) one gets

$$f(r; v^{(1)}(r)) = \delta(\tilde{r}-r')/4\pi\tilde{r}^2 \equiv f(r; r').$$

Thus

$$f(r, r') = -\int dr \frac{2}{(rR^{(0)}(r))^2} \int_r^\infty d\tilde{r} \left(\frac{\delta(\tilde{r}-r')}{4\pi\tilde{r}^2} - \frac{(R^{(0)}(r))^2}{4\pi} \right) (\tilde{r}R^{(0)}(\tilde{r}))^2 + C, \\ f(r, r') = \frac{1}{4\pi} (R^{(0)}(r))^2 \left(-\int dr \frac{2}{(rR^{(0)}(r))^2} \theta(r'-r) + \int dr \frac{2}{(rR^{(0)}(r))^2} \int_r^\infty d\tilde{r} (\tilde{r}^2 R^{(0)}(\tilde{r}))^2 \right) + C.$$

This integral can be obtained analytically, e.g., with MATHEMATICA.²⁴ It is:

$$f(r, r') = \frac{1}{4\pi} \left[-2 \frac{e^{-2r'}}{r} + 4re^{-2r'} - 4e^{-2r'} \text{Ei}(2r_{<}) + 4e^{-2r'} \ln r + \frac{2}{r} \min[1, e^{2(r-r')}] \right] + C, \quad (C2)$$

where $\text{Ei}(x) = -\int_{-\infty}^x e^{-t}/t dt$, and $r_{<}$ is $\min(r, r')$. The constant C is determined by the requirement of orthogonality between $\Psi^{(0)}$ and $\Psi^{(1)}$:

$$\int (R^{(0)}(r))^2 f(r) r^2 dr = 0,$$

yielding

$$C = \frac{e^{-2r'}}{4\pi r'} [-2 + 4r'^2 + r'(-14 + 8\gamma + \ln 256) + 4r' \ln r'], \quad (C3)$$

where γ is Euler's constant ($\gamma \approx 0.5772156649$). The first-order density change and thus $\chi_r(r, r')$ is $2(R^{(0)}(r))^2(f/4\pi)$, using Eqs. (C2) and (C3) one gets

$$\chi(r_{<}, r_{>}) = \frac{e^{-2(r_{<}+r_{>})}}{\pi^2 r_{<} r_{>}} [- (r_{<} + r_{>}) + r_{>} e^{2r_{<}} + r_{<} r_{>} \{-7 + 4\gamma + 2(r_{<} + r_{>}) - 2 \text{Ei}(2r_{<}) + \ln 16 + 2 \ln(r_{<} r_{>})\}].$$

¹F. Hohenberg and W. Kohn, Phys. Rev. B **136**, 864 (1964).

²W. Kohn and L. Sham, Phys. Rev. A **140**, 1133 (1965).

³J. Harris and R. Jones, J. Phys. F: Met. Phys. **4**, 1170 (1974).

⁴R. Q. Hood, M. Y. Chou, A. J. Williamson, G. Rajagopal, R. J. Needs, and W. M. C. Foulkes, Phys. Rev. Lett. **78**, 3350 (1997).

⁵R. Q. Hood, M. Y. Chou, A. J. Williamson, G. Rajagopal, and R. J. Needs, Phys. Rev. B **57**, 8972 (1998).

⁶A. Savin, F. Colonna, and J.-M. Teuler, in *Electronic Density Functional Theory: Recent Progress and New Directions*, edited by M. Das, G. Vignale, and J. Dobson (Plenum, New York, 1998).

⁷D. Langreth and J. Perdew, Solid State Commun. **17**, 1425 (1975).

⁸O. Gunnarsson and B. I. Lundqvist, Phys. Rev. B **13**, 4274 (1976).

⁹D. P. Joubert and G. P. Srivastava, J. Chem. Phys. **109**, 5212 (1998).

¹⁰F. Colonna and A. Savin, J. Chem. Phys. **110**, 2828 (1999).

¹¹D. Frydel, W. M. Terilla, and K. Burke, J. Chem. Phys. **112**, 5292 (2000).

¹²E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).

¹³D. Mearns and W. Kohn, Phys. Rev. A **35**, 4796 (1987).

¹⁴S. Hamel, M. E. Casida, and D. R. Salahub, J. Chem. Phys. (submitted).

¹⁵W. H. E. Schwarz and B. Müller, Chem. Phys. Lett. **166**, 621 (1990).

¹⁶D. E. Hoch and J. E. Harriman, J. Chem. Phys. **102**, 9590 (1995).

¹⁷E. Zaremba, J. Phys.: Condens. Matter **2**, 2479 (1990).

¹⁸O. V. Gritsenko, S. J. A. van Gisbergen, A. Gorling, and E. J. Baerends, J. Chem. Phys. **113**, 8478 (2000).

¹⁹S. J. A. van Gisbergen, P. R. T. Schipper, O. V. Gritsenko, E. J. Baerends, J. G. Snijders, B. Champagne, and B. Kirtman, Phys. Rev. Lett. **83**, 694 (1999).

²⁰R. G. Parr and W. Yang, Annu. Rev. Phys. Chem. **46**, 701 (1995).

²¹H. F. Hameka, J. Chem. Phys. **47**, 2728 (1967).

²²A. Dalgarno and J. T. Lewis, Proc. R. Soc. London, Ser. A **109**, 70 (1955).

²³W. H. Young and N. H. March, Phys. Rev. **109**, 1854 (1958).

²⁴S. Wolfram, *The Mathematica Book* (Wolfram Media/Cambridge University Press, Cambridge, 1996).