Asymptotic Behavior of the Kohn-Sham Exchange Potential

Fabio Della Sala* and Andreas Görling
Lehrstuhl für Theoretische Chemie, Technische Universität München, 85747 Garching, Germany

(Received 21 August 2001; published 27 June 2002)

The Kohn-Sham exchange potential of finite systems is shown to approach different asymptotic limits on nodal surfaces of the energetically highest-occupied orbital than in other regions. This leads to barrier-well structures in the near asymptotic region, which have a strong influence on virtual orbitals and thus on excitation energies. Common approximations for the exchange potential do not exhibit these features. These asymptotic structures, however, can be correctly described by effective exact-exchange methods. Conditions for the presence of an asymptotic barrier well in the full exchange-correlation potential are discussed.

DOI: 10.1103/PhysRevLett.89.033003 PACS numbers: 31.15.Ew, 32.80.Rm

The accuracy and thus the usefulness of the widely employed Kohn-Sham (KS) method of density-functional theory (DFT) depends on the quality of the approximations for the exchange-correlation (XC) functionals [1,2]. The development of such approximate XC functionals for a long time focused on optimizing the XC energy which is the crucial quantity in the KS treatment of electronic ground states. With the introduction of time-dependent DFT (TDDFT) [3,4] for the treatment of excitation energies and time-dependent phenomena the quality of approximate XC potentials became more important because the latter determine KS orbitals and their eigenvalues, the input data for TDDFT approaches. There is also a growing interest in employing KS orbitals and eigenvalues in procedures combining DFT and standard many-body or quantum chemistry methods [5,6]. KS orbitals and their eigenvalues, in particular if unoccupied, depend sensitively on the XC potential. Common XC potentials are not free of Coulomb self-interactions, thus do not exhibit the correct asymptotic behavior [1,2] in finite systems, and result in qualitatively wrong KS spectra which in turn lead to large errors in TDDFT methods.

Recently various asymptotically corrected (AC) approximate XC potentials were developed [7–10] which, far from the system, approach $-1/r$ with r being the distance from the center of the nuclear charges. Indeed it was shown in Refs. [11,12] that for finite systems the KS potential $v_s(\mathbf{r})$ approaches $-1/r$ far outside. The KS potential is given by $v_s(\mathbf{r}) = v_{\rm nuc}(\mathbf{r}) + u(\mathbf{r}) + v_x(\mathbf{r}) + v_c(\mathbf{r})$ with $v_{\rm nuc}(\mathbf{r})$, $u(\mathbf{r})$, $v_x(\mathbf{r})$, and $v_c(\mathbf{r})$ representing the electrostatic potential of the nuclei, the Coulomb potential, the exchange potential, and the correlation potential, respectively. Because the electrostatic potential of the nuclei and the Coulomb potential cancel each other asymptotically for neutral systems and because the correlation potential is assumed to be short range [12], the KS and exchange potentials are assumed to exhibit the same $-1/r$ asymptotic behavior in atoms or molecules.

In this Letter we show that this is not true in general. In directions where the energetically highest-occupied molecular orbital (HOMO) has a nodal surface in the asymptotic region the exchange potential of molecules is shown to approach a different value than in other directions. Thus if the, at first, undefined additive constant contained in $v_x(\mathbf{r})$ is, as usual, chosen such that the exchange potential approaches $-1/r$ in "normal" directions then it approaches $C - 1/r$ on nodal surfaces of the HOMO with C being a constant. In systems with a degenerate HOMO, $v_x(\mathbf{r})$ approaches $C - 1/r$ only in the direction where the sum of the electron densities of all HOMOs is zero in the asymptotic region. For simplicity we will focus here on closed shell systems with a nondegenerate HOMO and real valued orbitals. All results, however, are generally valid. A nodal surface is a region of zero measure. Therefore $v_x(\mathbf{r})$ approaches $C - 1/r$ only in regions of zero measure. However, because the exchange potential, except for $r \to \infty$, is continuous the different asymptotic limits lead to strong anisotropies and barrier-well structures in the near asymptotic region which have a strong effect on the unoccupied KS orbitals. Because present AC exchange potentials neither exhibit the correct asymptotic limits nor the anisotropies and barrier-well structures, we here calculate the latter with a recently introduced effective exact-exchange (EXX) method [13].

As a first step we now show that the assumption that both $v_s(\mathbf{r})$ and $v_x(\mathbf{r})$ asymptotically approach $-1/r$ leads to a contradiction. If $v_s(\mathbf{r})$ approaches $-1/r$ for $r \to \infty$ then the asymptotic behavior of the KS orbitals $\phi_b(\mathbf{r}_l)$ with eigenvalues ϵ_b is given by [14]

$$\phi_b(\mathbf{r}_l) \overset{r_l \to \infty}{\to} e^{-\beta_b r_l}. \tag{1}$$

with $\beta_b = \sqrt{-2\epsilon_b}$ on points $\mathbf{r}_l$ on a line l through the center of nuclear charges of the molecule. It is sufficient here to consider in asymptotic expressions only the exponential and to disregard any prefactors containing powers of r. The orbitals ϕ_b shall be occupied KS orbitals which do not have a nodal surface in the asymptotic region along the line l. The set of these orbitals shall be called B_l. The exact-exchange potential $v_x(\mathbf{r})$ solves the EXX equation which can be recast in the form [14]

$$\sum_{a=1}^{\mathrm{occ}} \psi_a([v_x];\mathbf{r})\phi_a(\mathbf{r}) = 0 \tag{2}$$

with

$$\psi_a([v_x];\mathbf{r}) = \sum_{i\neq a}^{all} \frac{\langle \phi_a | \hat{v}_x - \hat{v}_x^{\mathrm{NL}} | \phi_i \rangle}{\epsilon_a - \epsilon_i}\,\phi_i(\mathbf{r}) . \tag{3}$$

In Eq. (2), $\hat{v}_x^{\mathrm{NL}}$ is a nonlocal exchange operator of the form of the Hartree-Fock exchange operator but constructed from KS orbitals. The quantity $\psi_a([v_x];\mathbf{r})$ solves the inhomogeneous differential equation [14]

$$\begin{aligned}\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}) - \epsilon_a\right)&\psi_a([v_x];\mathbf{r}) \\ &= -v_x(\mathbf{r})\phi_a(\mathbf{r}) + [\hat{v}_x^{\mathrm{NL}}\phi_a](\mathbf{r}) + D_a\phi_a(\mathbf{r})\end{aligned} \tag{4}$$

with $D_a = \langle \phi_a | \hat{v}_x - \hat{v}_x^{\mathrm{NL}} | \phi_a \rangle$.

From the asymptotic decay of the orbitals, Eq. (1), it follows that the three terms on the right-hand side of Eq. (4) asymptotically behave as

$$v_x(\mathbf{r}_l)\phi_b(\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} v_x(\mathbf{r}_l)e^{-\beta_b r_l}, \tag{5}$$

$$[\hat{v}_x^{\mathrm{NL}}\phi_b](\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} e^{-\beta_M r_l}, \tag{6}$$

$$D_b\phi_b(\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} e^{-\beta_b r_l} \tag{7}$$

for points on the line l. In Eq. (6), M refers to the energetically highest-occupied orbital in the set B_l. If $b \neq M$ then Eq. (4) asymptotically assumes the form

$$\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}_l) - \epsilon_b\right)\psi_b([v_x];\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} e^{-\beta_M r_l}. \tag{8}$$

The asymptotic decay of $\psi_b([v_x];\mathbf{r}_l)$ is given by the decay of the *particular* solution of Eq. (8):

$$\psi_b([v_x];\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} e^{-\beta_M r_l}, \qquad b \neq M . \tag{9}$$

The solutions of the *homogeneous* equation corresponding to Eq. (4) do not contribute to $\psi_b([v_x];\mathbf{r})$ and its asymptotic decay because one of the homogeneous solutions is ϕ_b which is explicitly excluded from the sum (3) defining $\psi_b([v_x];\mathbf{r})$ and the other one is exponentially increasing with $e^{\beta_b r_l}$ and cannot be built by the sum (3).

The asymptotic form of $\psi_M([v_x];\mathbf{r}_l)$ follows from the asymptotic form of the EXX equation (2) which leads to

$$\psi_M([v_x];\mathbf{r}_l) = -\frac{1}{\phi_M(\mathbf{r}_l)} \sum_{b\neq M} \psi_b([v_x];\mathbf{r}_l)\phi_b(\mathbf{r}_l) . \tag{10}$$

With Eqs. (1) and (9) the asymptotic decay of $\psi_M([v_x];\mathbf{r}_l)$ is given by

$$\psi_M([v_x];\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} e^{-\beta_{M-K} r_l}, \tag{11}$$

where $M - K$ with $K \geq 1$ indicates the second-highest-occupied orbital in the set B_l. Note that the asymptotic form of $\psi_M([v_x];\mathbf{r}_l)$ cannot be obtained from Eqs. (4)–(7) because in this case $\beta_b = \beta_M$ and all three terms given by the right-hand sides of Eqs. (5)–(7) contribute to the asymptotic behavior of the right-hand side of Eq. (4) and it cannot be ruled out that the three terms cancel each other. Equation (11) shows that this indeed must be the case.

The asymptotic form of the exact-exchange potential is obtained from Eq. (4) for the orbital M on the line l,

$$\begin{aligned} v_x(\mathbf{r}_l) = D_M &+ \frac{[\hat{v}_x^{\mathrm{NL}}\phi_M](\mathbf{r}_l)}{\phi_M(\mathbf{r}_l)} \\ &- \frac{1}{\phi_M(\mathbf{r}_l)}\left(-\frac{\nabla^2}{2} + v_s(\mathbf{r}_l) - \epsilon_M\right)\psi_M([v_x];\mathbf{r}_l) .\end{aligned} \tag{12}$$

Because of Eqs. (1) and (11) the last term on the right-hand side of Eq. (12) vanishes asymptotically as $e^{-(\beta_{M-K}-\beta_M)r_l}$. Since $[\hat{v}_x^{\mathrm{NL}}\phi_M](\mathbf{r}_l)/\phi_M(\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} -1/r_l$ the exact-exchange potential asymptotically behaves as

$$v_x(\mathbf{r}_l) \overset{r_l\to\infty}{\longrightarrow} D_M - \frac{1}{r_l} . \tag{13}$$

Thus the exact-exchange potential $v_x(\mathbf{r})$ will approach the constant $D_M = \langle \phi_M | \hat{v}_x - \hat{v}_x^{\mathrm{NL}} | \phi_M \rangle$ on the line l with M being an energetically highest-occupied orbital in the set B_l. We now fix the, so far, undefined additive constant in $v_x(\mathbf{r})$ by requiring that $D_N = \langle \phi_N | \hat{v}_x - \hat{v}_x^{\mathrm{NL}} | \phi_N \rangle = 0$ with ϕ_N being the HOMO. Then $v_x(\mathbf{r})$ approaches $-1/r$ along all directions where $\phi_N(\mathbf{r})$ does not have a nodal surface in the asymptotic region. Along a direction $\hat{\mathbf{r}}_N$ which belongs to a nodal surface of the HOMO, v_x will approach $D_M - 1/r$, where M indicates the highest-occupied orbital which does not have a nodal surface in the asymptotic region in the direction $\hat{\mathbf{r}}_N$.

Thus if the KS potential v_s exhibits the same asymptotic behavior as v_x it also must approach $D_M - 1/r$ along directions $\hat{\mathbf{r}}_N$, where the HOMO has a nodal surface in the asymptotic region. This is a contradiction to the assumption that $v_s(\mathbf{r})$ approaches $-1/r$ everywhere if $r \to \infty$. If the correlation potential is short range as believed [12] and thus does not cancel the exchange potential in the directions $\hat{\mathbf{r}}_N$ (see also below), then the contradiction is solved if v_s indeed approaches $D_M - 1/r$ along $\hat{\mathbf{r}}_N$ because the above investigation on the asymptotic behavior of v_x remains valid if, on a line l, the KS potential v_s approaches $D_M - 1/r$ instead of $-1/r$ as originally assumed. The only change is that, along such a line l, $\beta_b = \sqrt{-2(\epsilon_b - D_M)}$ instead of $\beta_b = \sqrt{-2\epsilon_b}$ (note that $D_M > 0$ in actual systems). The present results suggest to reconsider earlier work [11,12] on the asymptotic of v_s.

We emphasize that the finding that v_x asymptotically approaches a constant is not a rare special case but is the case usually encountered in molecules. The HOMOs of real molecules with more than two electrons have nodal planes. Only if these nodal planes do not reach into the asymptotic region can v_x asymptotically approach $-1/r$

everywhere. This, for example, is the case in atoms which have *s* orbitals with spherical nodal surfaces as HOMOs. In the case of degeneracies it may happen that the sum of the electron densities of the HOMOs is never zero in the asymptotic region even though the individual HOMOs have nodal surfaces reaching into the asymptotic region. An example is noble gas atoms in which the HOMOs are a set of degenerate *p* orbitals.

Recently methods to construct the exact-exchange potential of molecules were introduced [15,16]. For finite systems these methods unfortunately suffer from numerical problems which prevent an investigation of the asymptotic region of the exchange potential. Very recently we proposed [13] an effective exact-exchange KS method, the localized Hartree-Fock (LHF) method, which determines and uses an almost exact-exchange potential, the LHF exchange potential $v_x^{\mathrm{LHF}}(\mathbf{r})$ given by

$$v_x^{\mathrm{LHF}}(\mathbf{r}) = v_x^S(\mathbf{r}) + v_x^{\mathrm{cor}}(\mathbf{r}). \tag{14}$$

In Eq. (14), $v_x^S(\mathbf{r})$ is the Slater potential and $v_x^{\mathrm{cor}}(\mathbf{r})$ is a correction term given by

$$v_x^{\mathrm{cor}}(\mathbf{r}) = \frac{2}{\rho(\mathbf{r})} \sum_{(a,b)\neq(N,N)}^{\mathrm{occ}} C_{ab}\phi_a(\mathbf{r})\phi_b(\mathbf{r}), \tag{15}$$

with $C_{ab} = C_{ba} = \langle\phi_a|\hat{v}_x^{\mathrm{LHF}} - \hat{v}_x^{\mathrm{NL}}|\phi_b\rangle$ and $\rho(\mathbf{r})$ denoting the electron density. The sum in Eq. (15) runs over all pairs of occupied orbitals, except the one containing two times the HOMO. The right-hand side of Eq. (15) contains in the constants C_{ab} the LHF exchange potential v_x^{LHF}. Thus v_x^{LHF} has to be determined self-consistently in the LHF KS procedure. If the terms with $a \neq b$ are neglected in Eq. (15) then the approximation of the exchange potential due to Krieger, Li, and Iafrate (KLI) [17] is obtained.

The LHF/KLI exchange potential is well suited to investigate the asymptotic behavior of the exchange potential of molecules for two reasons: (i) The LHF/KLI exchange potentials exhibit the same limits for $r \to \infty$ as the exact-exchange potential because the Slater potential always approaches $-1/r$, and the correction term [due to the asymptotic behavior of the orbitals, Eq. (1)] exponentially approaches zero, except on nodal surfaces of the HOMO where it approaches $D_M = C_{MM}$. (ii) The asymptotic region of the LHF/KLI potential can be calculated with virtually no numerical errors, using a recently introduced technique [18] based on asymptotic continuations of orbitals. We here applied it within the program package, Turbomole [19], to various small and medium sized molecules. As a representative example, we here discuss exchange-only results obtained for benzene. The benzene molecule with D_{6h} symmetry and bond distances of $d_{C\text{-}C} = 1.393$ Å and $d_{C\text{-}H} = 1.084$ Å is located in the *xy* plane with one of the *H-C-C-H* connection axes located along the *y* axis. Results for other molecules and technical details will be published elsewhere [18].

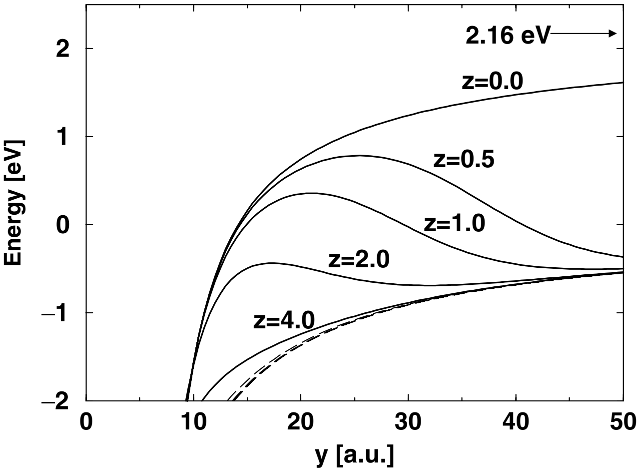

FIG. 1. LHF exchange potential of benzene in the *yz* plane along lines parallel to the *y* axis. The dashed lines represent the AC exchange potential along the same lines.

In Fig. 1 the $v_x^{\mathrm{LHF}}(\mathbf{r})$ is plotted along the *y* axis and along lines which are obtained by shifting upwards the *y* axis parallel in the *yz* plane to different values of *z*. Because in benzene the HOMOs are a set of two degenerate π orbitals which both have a nodal plane in the molecular plane, i.e., in the *xy* plane, the exchange potential $v_x(\mathbf{r})$ must approach a constant in this plane. Indeed Fig. 1 shows that along the *y* axis $v_x(\mathbf{r})$ approaches the constant value 2.16 eV. Along the other lines displayed in Fig. 1 the HOMOs of benzene do not have a nodal plane and therefore $v_x(\mathbf{r})$ must approach $-1/r$ and eventually zero. This is indeed the case. However, the exchange potential is continuous except for $r \to \infty$. Therefore the closer a line lies at the *xy* plane the later the $-1/r$ behavior is reached and the longer the behavior of the exchange potential resembles the one on the *y* axis. As a result barrier-well structures are formed in the near asymptotic region in the vicinity of the *xy* plane, up to a distance of 2.0 a.u. from the plane. The dashed lines at the bottom of Fig. 1 show the exchange potential as calculated in AC methods [9]: its shape is almost the same along the various lines, whereas the LHF potential strongly changes with *z*.

Table I displays data on KS eigenvalues of benzene obtained in exchange-only KS calculations with different exchange potentials. The KS spectra obtained with exchange potentials from the local density approximation (LDA) [2] and a generalized gradient approximation (GGA) [20] contain only two bound unoccupied orbitals due to the completely wrong asymptotic behavior of these exchange potentials. The AC exchange potential due to van Leeuwen and Baerends [7] (LB94) leads to a much improved eigenvalue spectra with a large number of bound unoccupied orbitals. However, shifts of more than 1 eV compared to the LHF values are observed. In the last column of Table I (LHF-AC) we report the shifts in the KS eigenvalues if the LHF potential in the asymptotic region

TABLE I. KS eigenvalues (eV) for different exchange potentials. Column "LHF" shows LHF eigenvalues; other columns (for definitions, see text) show differences to LHF values.

		ε	$\Delta\varepsilon$			
Sym.	Occ	LHF	LDA	GGA	LB94	LHF-AC
$3a_{2u}$	0	-0.96	–	–	-0.15	-0.30
$4e_{2g}$	0	-1.03	–	–	-1.34	-1.03
$6a_{1g}$	0	-1.08	–	–	-0.26	-0.50
$2e_{1g}$	0	-1.17	–	–	-0.38	-0.66
$5a_{1g}$	0	-1.59	–	–	-0.69	-0.45
$4e_{1u}$	0	-1.78	–	–	-1.25	-0.82
$2a_{2u}$	0	-1.92	–	–	-0.39	-0.49
$4a_{1g}$	0	-2.64	2.50	2.34	-1.11	-0.49
$1e_{2u}$	0	-3.92	3.65	3.65	-1.28	-0.02
$1e_{1g}$	2	-9.16	3.82	3.82	-1.01	-0.01
$3e_{2g}$	2	-11.10	4.12	3.76	-0.40	-0.01
$1a_{2u}$	2	-12.00	3.90	3.94	-0.85	-0.01
$\cdots$	2	$\cdots$	$\cdots$	$\cdots$	$\cdots$	-0.01

(as defined in Ref. [18]) is replaced by a $-1/r$ behavior (the one in Ref. [9]). While the occupied orbital and the lowest-unoccupied molecular orbital are almost unaffected, all the virtual orbitals are strongly shifted. The orbitals which do not have a nodal plane in the molecular plane (e.g., $4e_{2g}$, $4e_{1u}$) are shifted particularly strong. This clearly shows that the proper treatment of the asymptotic region has a strong influence on the diffuse unoccupied orbital. We calculated excitation energies from LHF orbitals using a simple static exchange-only LDA kernel and we have found good agreement with experiments both for valence and Rydberg excitation [21], whereas when using LHF-AC orbitals, the Rydberg excitation energies are significantly underestimated. This shows the importance of LHF asymptotic barrier-well structures for the calculation of high-lying excitation energies.

The findings of this work can be generalized to the full XC potential $v_{xc}(\mathbf{r})$: $v_{xc}(\mathbf{r})$ will asymptotically approach the constant $\langle\phi_M|\hat{v}_{xc} - \hat{u}_M|\phi_M\rangle$ if

$$u_b(\mathbf{r}_l)\phi_b(\mathbf{r}_l) = \frac{dE_{xc}}{d\phi_b(\mathbf{r}_l)} \overset{r_l\to\infty}{\to} e^{-\beta_M r_l}. \qquad (16)$$

Condition (16) is the analog of Eq. (6). In order to assess its validity, we note that, under a quasiparticle approximation to the linear response of the Sham-Schlüter equation [22], condition (16) takes the form

$$\hat{\Sigma}_{xc}(\epsilon_b)\phi_b(\mathbf{r}_l) \overset{r_l\to\infty}{\to} e^{-\beta_M r_l}, \qquad (17)$$

where $\hat{\Sigma}_{xc}(\epsilon)$ is the nonlocal energy-dependent self-energy operator. Condition (17) is well satisfied for the presently considered self-energy expressions.

This indicates that asymptotic barrier wells are present even in the full XC potential.

---

*Permanent address: National Nanotechnology Laboratories, INFM-Dipartimento di Ingegneria dell'Innovazione, Università degli Studi di Lecce, Via per Arnesano, 73100 Lecce, Italy.

[1] R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecules* (Oxford University Press, Oxford, 1989).

[2] W. Koch and M. C. Holthausen, *A Chemist's Guide to Density Functional Theory* (Wiley-VCH, New York, 2000).

[3] E. K. U. Gross, J. F. Dobson, and M. Petersilka, in *Density Functional Theory II,* edited by R. F. Nalewajski, Springer Series in Topics in Current Chemistry Vol. 181 (Springer, Berlin, 1996), p. 81.

[4] M. E. Casida, in *Recent Advances in Density Functional Methods,* edited by D. P. Chong (World Scientific, Singapore, 1995), Vol. 1, p. 155.

[5] L. Veseth, J. Chem. Phys. **114**, 8789 (2001).

[6] T. Hupp, B. Engels, F. Della Sala, and A. Görling, Chem. Phys. Lett. (to be published).

[7] R. van Leeuwen and E. J. Baerends, Phys. Rev. A **49**, 2421 (1994).

[8] P. R. T. Schipper, O. V. Gritsenko, S. J. A. van Gisbergen, and E. J. Baerends, J. Chem. Phys. **112**, 1344 (2000).

[9] D. J. Tozer and N. C. Handy, J. Chem. Phys. **109**, 10 180 (1998).

[10] M. E. Casida and D. R. Salahub, J. Chem. Phys. **113**, 8918 (2000).

[11] M. Levy, J. P. Perdew, and V. Sahni, Phys. Rev. A **30**, 2745 (1984), and references therein.

[12] C.-O. Almbladh and U. von Barth, Phys. Rev. B **31**, 3231 (1985).

[13] F. Della Sala and A. Görling, J. Chem. Phys. **115**, 5718 (2001).

[14] T. Kreibich, S. Kurth, T. Grabo, and E. K. U. Gross, Adv. Quantum Chem. **33**, 31 (1999).

[15] A. Görling, Phys. Rev. Lett. **83**, 5459 (1999).

[16] S. Ivanov, S. Hirata, and R. J. Bartlett, Phys. Rev. Lett. **83**, 5455 (1999).

[17] J. B. Krieger, Y. Li, and G. J. Iafrate, Phys. Rev. A **46**, 5453 (1992).

[18] F. Della Sala and A. Görling, J. Chem. Phys. **116**, 5374 (2002).

[19] R. Ahlrichs *et al.,* Chem. Phys. Lett. **162**, 165 (1989).

[20] A. D. Becke, Phys. Rev. A **38**, 3098 (1988).

[21] F. Della Sala and A. Görling, Int. J. Quantum Chem (to be published).

[22] M. E. Casida, Phys. Rev. A **51**, 2005 (1995).