New KS Method for Molecules Based on an Exchange Charge Density Generating the Exact Local KS Exchange Potential

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A new all-electron Kohn-Sham method for molecules and clusters is introduced and applied. The local Kohn-Sham exchange potential and the exchange energy are treated exactly. The method yields high quality one-particle spectra. An exchange-correlation charge density which generates the exchange-correlation potential is introduced. It may turn out to be of great interpretative value. Within the new Kohn-Sham method the exchange part of this density is constructed.

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The Kohn-Sham (KS) formalism of density-functional theory (DFT) [1,2] has become the most widely employed approach for the theoretical treatment of electronic systems. Despite their great success, KS methods employing present state-of-the-art approximations to the exchange-correlation functionals exhibit serious shortcomings which severely limit their applicability. Today's KS implementations are incapable of describing the simplest electronic system, the hydrogen atom, exactly, and they fail in the treatment of most anions. Moreover, they yield unphysical one-particle spectra. The gap between the energetically highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is much too small. In neutral systems only a few bound unoccupied states instead of a Rydberg series are obtained. Because it has been shown recently that KS eigenvalue differences are well-defined approximations for excitation energies [3,4], the KS one-particle spectrum should reflect the physical excitation spectrum. Even more important, KS orbitals and eigenvalues, occupied as well as unoccupied ones, are the input for time-dependent DFT, a theory which, in principle, yields exactly all of the response properties of electronic systems including exact excitation energies. At present, however, the accuracy and applicability of time-dependent DFT methods is limited by the deficiencies of the KS one-particle spectrum.

The described shortcomings of KS methods employing the present approximate exchange-correlation functionals all originate in the incomplete cancellation of the unphysical self-interactions contained in the Coulomb energy and potential. As the most important consequence of this self-interaction, the effective potential in the KS equations falls off too rapidly and does not equal asymptotically the electrostatic potential of a single positive charge ($1/r$ potential) which an electron should experience far from the system. Because of this too rapid decay of the effective KS potential, no Rydberg series exists in the KS one-particle spectrum and the potential is not attractive enough to bind the additional electron in an anion. The Coulomb self-interactions are not canceled by exchange interactions because the latter are approximated in present KS procedures. Satisfying remedies against the self-interaction problem are not available at present. Self-interaction corrections lead to different Hamiltonian operators for the KS orbitals and are not convincing from a formal point of view. Recently suggested approximate exchange and exchange-correlation potentials, constructed to yield the correct asymptotic behavior, are either not accompanied by a corresponding approximate density functional for the energy [5] or contain a large number of empirical constants [6].

The ultimate way to avoid the Coulomb self-interaction problem, of course, is to treat the KS exchange exactly. This amounts to the construction of the exact *local* KS exchange potential which has to be distinguished from a nonlocal exchange potential as it appears in the Hartree-Fock (HF) formalism. A consistent exact treatment of the exchange energy is straightforward. The exchange energy E_x is known in terms of the KS orbitals $\phi_a(\mathbf{r})$. The expression for E_x has the same form as the HF exchange energy and thus can be evaluated with the same techniques. Note that KS and HF exchange energies differ because the orbitals entering the expression for E_x are different in the two formalisms.

A second reason to develop an exact-exchange (EXX) KS method emerges from the wish to develop DFT in a systematic fashion. Thomas-Fermi methods [1,2] can be considered as the first generation of DFT procedures in which all energies have to be approximated, except for the Coulomb energy and the electron-nuclei interaction energy. Present KS methods represent a second generation of DFT procedures. Here, additionally, a large part of the kinetic energy, the noninteracting kinetic energy, is treated exactly. The next step in a systematic development of DFT is to treat exactly exchange interactions. Then, for all energies and potentials of zeroth and first order in the electron-electron interaction, approximations are avoided. Approximate density functionals are only necessary in order to take into account the higher order terms which represent the correlation energy and potential. EXX methods therefore represent a third generation of DFT methods.

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A long known EXX procedure is the optimized potential method (OPM) [7]. As a numerical grid method the OPM is restricted to spherical, i.e., atomic, systems. A basis set EXX method was suggested in Ref. [8] and recently implemented on the basis of plane wave basis sets [9]. The resulting plane wave EXX procedure is *de facto* limited to periodic systems. Moreover, it relies on the introduction of pseudopotentials and thus is not an all-electron method. For molecules and solids, several approximations towards an EXX method were introduced recently [10–13]. They either require drastic approximations concerning the form of the KS potential (the atomic sphere approximation) [10] or introduce severe approximations during the construction of the exchange potential (the energy differences between occupied and unoccupied KS orbitals are all assumed to be equal) [11–13].

In this Letter an all-electron EXX method for molecules and clusters based on Gaussian or Slater basis sets is presented. It is generally applicable, it can easily be implemented in existing quantum chemistry codes, and the computational effort it requires is comparable to that of HF procedures. For simplicity the formalism will be described for the case of nonspin-polarized systems. The numerical examples contain nonspin-polarized as well as spin-polarized molecules.

The exchange potential $v_x(\mathbf{r})$ obeys the EXX equation [7,8,14]

$$\int d\mathbf{r}'\, X(\mathbf{r},\mathbf{r}')v_x(\mathbf{r}') = \sum_a^{\text{occ}} \sum_s^{\text{unocc}} \phi_a^\dagger(\mathbf{r})\phi_s(\mathbf{r}) \times \frac{\langle\phi_s|\hat{v}_x^{\text{NL}}|\phi_a\rangle}{\varepsilon_a - \varepsilon_s} + \text{c.c.} \quad (1)$$

In the EXX equation, ϕ_a and ϕ_s denote occupied and unoccupied KS orbitals, ε_a and ε_s represent the corresponding KS eigenvalues. By $\hat{v}_x^{\text{NL}}$ a nonlocal exchange operator is denoted. It has the form of the HF exchange operator but is built from KS orbitals. Its kernel $v_x^{\text{NL}}(\mathbf{r},\mathbf{r}')$ is given by $\sum_a^{\text{occ}} \phi_a^\dagger(\mathbf{r})\phi_a(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$. The symbol X designates the response function of the KS system,

$$X(\mathbf{r},\mathbf{r}') = \sum_a^{\text{occ}} \sum_s^{\text{unocc}} \frac{\phi_a^\dagger(\mathbf{r}')\phi_s(\mathbf{r}')\phi_s^\dagger(\mathbf{r})\phi_a(\mathbf{r})}{\varepsilon_a - \varepsilon_s} + \text{c.c.} \quad (2)$$

The approach of Ref. [8] for solving the EXX equation which underlies the plane wave EXX method [9] is based on directly expanding the equation into a basis set $\{f_k(\mathbf{r})\}$, an auxiliary basis set in addition to the basis set for the KS orbitals. The exchange potential is then obtained as a linear combination of the auxiliary basis functions. However, two problems impair the implementation of this approach to solve the EXX equation if the standard types of basis sets of molecular physics, Gaussian or Slater-type basis sets, shall be employed. Firstly, the EXX equation yields the exchange potential v_x only up to an additive constant: if v_x solves the EXX equation, so does $v_x + c$ with c being a constant. Because v_x is defined only up to an additive constant if the particle number is fixed, this is consistent with the formalism. It does, however, mean that one has, for numerical reasons, to exclude all those linear combinations of basis functions from the auxiliary basis set which are close to a constant function. Linear combinations of Gaussian- or Slater-type functions decay exponentially and thus never equal exactly a constant function. Therefore, if a linear combination is excluded from the auxiliary basis set for numerical reasons also some physical information on v_x is lost.

Secondly, the long-range asymptotic $1/r$ behavior (or $1/r + c$ behavior) of the exchange potential cannot be represented by finite Gaussian or Slater-type basis sets due to the short-range exponential decay of Gaussian- and Slater-type functions. This problem cannot be avoided by simply increasing the size of the auxiliary basis set because, if the auxiliary basis set is large compared to the basis set for the KS orbitals, some linear combinations of the auxiliary basis set will not couple to the response operator ($\langle\phi_a|f_k|\phi_s\rangle = 0$, for all a, s, for unbalanced basis sets) and numerical instabilities are introduced.

The approach to determine the exchange potential introduced in this work starts by selecting the specific solution of the EXX equation which vanishes at infinity, i.e., $v_x(\infty) = 0$. From now on, v_x shall designate exclusively this specific solution. For this choice of $v_x(\infty)$ the KS eigenvalue of the HOMO equals the negative of the ionization energy of the system. Moreover, and this is the crucial point, the Poisson equation $\rho_x(\mathbf{r}) = (-1/4\pi)\nabla^2 v_x(\mathbf{r})$ leads to a density $\rho_x(\mathbf{r})$ which shall be called the exchange charge density. Thus *the exchange charge density is defined as the charge distribution whose electrostatic potential is the exchange potential*

$$v_x(\mathbf{r}) = \int d\mathbf{r}' \frac{\rho_x(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad (3)$$

In a similar way a correlation and a combined exchange-correlation charge density, ρ_c and ρ_{xc}, can be defined by replacing v_x in Eq. (3) by v_c or v_{xc}, respectively. Addition of the exchange-correlation charge density to the regular electron density yields an effective density which, via Poisson's equation, yields the Hartree plus the exchange-correlation potential, i.e., an effective density which incorporates all many-body effects. This effective density is the one which the electrons actually "see." It presumably may play an important role in the analysis and interpretation of electronic structures in the future.

Substitution of Eq. (3) into Eq. (1) leads to an EXX equation for the exchange charge density

$$\int d\mathbf{r}'d\mathbf{r}'' \frac{X(\mathbf{r},\mathbf{r}')\rho_x(\mathbf{r}'')}{|\mathbf{r}'-\mathbf{r}''|} = \sum_a^{\text{occ}} \sum_s^{\text{unocc}} \phi_a^\dagger(\mathbf{r})\phi_s(\mathbf{r}) \frac{\langle\phi_s|\hat{v}_x^{\text{NL}}|\phi_a\rangle}{\varepsilon_a - \varepsilon_s} + \text{c.c.} \quad (4)$$

Next the exchange charge density is expanded in an auxiliary basis set of Gaussian-type or Slater-type functions, $\rho_x(\mathbf{r}) = \sum_k c_k f_k(\mathbf{r})$. The EXX equation (4) is then also expanded in the auxiliary basis set employing the Coulomb norm. As result, the matrix equation $\mathbf{X}\mathbf{c} = \mathbf{t}$ for the vector $\mathbf{c}$ collecting the expansion coefficients of the exchange charge density is obtained. The elements $X_{k\ell}$ of the matrix $\mathbf{X}$ are given by

$$X_{k\ell} = \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4 \, \frac{f_k(\mathbf{r}_1) X(\mathbf{r}_2, \mathbf{r}_3) f_\ell(\mathbf{r}_4)}{|\mathbf{r}_1 - \mathbf{r}_2| \, |\mathbf{r}_3 - \mathbf{r}_4|}, \quad (5)$$

and the elements t_k of the vector $\mathbf{t}$ are given by

$$t_k = \sum_a^{\text{occ}} \sum_s^{\text{unocc}} \int d\mathbf{r}_1 d\mathbf{r}_2 \, \frac{f_k(\mathbf{r}_1) \phi_a^\dagger(\mathbf{r}_2) \phi_s(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \times \langle \phi_s | \hat{v}_x^{\text{NL}} | \phi_a \rangle + \text{c.c.} \quad (6)$$

The exchange potential is then obtained as

$$v_x(\mathbf{r}) = \sum_k c_k \int d\mathbf{r}' \, \frac{f_k(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|}. \quad (7)$$

The evaluation of Eqs. (5) and (6) leads to Coulomb matrix elements between one auxiliary and two orbital basis functions. Such matrix elements as well as the matrix elements $\langle \phi_s | \hat{v}_x^{\text{NL}} | \phi_a \rangle$ are available in standard computer codes.

Because the exchange charge density is unique, Eq. (4) has a unique solution. Thus the problem of removing linear combinations of basis functions which are close to a constant is no longer present. The exchange charge density has to obey the condition $\int d\mathbf{r} \, \rho_x(\mathbf{r}) = -1$ in order to yield an exchange potential with the correct asymptotic $1/r$ behavior. For Gaussian- as well as Slater-type functions the right-hand side of Eq. (7) asymptotically turns into $[\sum_k \int d\mathbf{r}' f_k(\mathbf{r}')]/r$. Thus the basis set representation (7) of the exchange charge automatically yields the correct asymptotic $1/r$ behavior provided the sum $\sum_k \int d\mathbf{r} f_k(\mathbf{r})$ correctly equals -1. In practice it turns out that the latter condition is not very accurately obeyed for numerical reasons. While this does not affect energies or other observables it does lead to an undesirable shift of the KS eigenvalues. Therefore the correct value of the integral $\sum_k \int d\mathbf{r} \, f_k(\mathbf{r})$ is enforced by changing the right-hand side of the matrix equation $\mathbf{X}\mathbf{c} = \mathbf{t}$ into $\mathbf{t} + \lambda\mathbf{n}$ with the elements n_k of the vector $\mathbf{n}$ being $\int d\mathbf{r} \, f_k(\mathbf{r})$ and with the Lagrange multiplier λ being $(-)(1 + \mathbf{n}^T \mathbf{X}^{-1} \mathbf{t})/(\mathbf{n}^T \mathbf{X}^{-1} \mathbf{n})$.

The introduced EXX method was applied to atoms and various small molecules including one anion. Matrix elements were evaluated by the programs PARAGAUSS [15] and GAMESS [16]. The employed uncontracted Gaussian basis sets [17] are large enough that errors in the calculated energies due to basis set incompleteness are negligible. All virtual orbitals were taken into account in the summations of Eqs. (1), (2), (4), and (6). Results for atoms from the present EXX implementation agree well with those from the optimized potential method of Ref. [11].

TABLE I. Atomization energies of molecules (kcal/mol).

System	EXX	EXX-LDA	EXX-PBE	LDA	PBE	Expt.
H_2	84	115	104	113	105	109
LiH	34	62	52	61	53	58
OH	69	96	94	124	110	107
FH	98	124	123	164	142	141
Li_2	4	21	17	24	20	24
LiF	92	120	116	163	144	139
CO	172	209	217	298	268	259
N_2	112	167	171	266	242	229
O_2	30	55	68	174	143	121
F_2	−42	−28	−21	80	53	39
NH_3	200	282	275	337	302	297
H_2O	156	210	207	266	234	232
CH_4	327	419	411	462	420	419
CN^-	188	237	246	-	-	240
Error[a]	64.46	26.31	26.15	27.54	6.77	-

[a] Mean absolute deviation (without data for CN^-).

In Table I, atomization energies calculated at experimental geometries [18] are listed. EXX, EXX-LDA, and EXX-PBE stand for exact exchange plus no correlation, plus local density approximation (LDA; Perdew-Wang parametrization [19]) for correlation, and plus the generalized gradient approximation according to Perdew, Burke, and Ernzerhof (PBE) [20] for correlation, respectively. By using LDA and PBE, results are labeled which were obtained with the LDA and the PBE approximation, respectively, for both exchange and correlation. The PBE approximation was chosen to represent generalized gradient approximations in general.

The results are as expected. Pure EXX atomization energies are very close to the corresponding HF values, listed, e.g., in Ref. [20]. All atomization energies

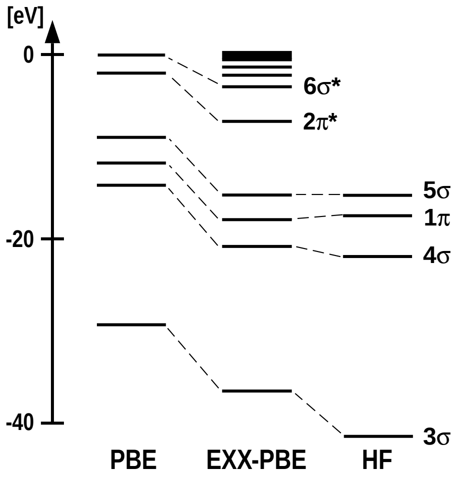

FIG. 1. Eigenvalue spectra of the valence and bond virtual KS orbitals of carbon monoxide. The labels indicating the symmetry and energetic ordering refer to the full spectrum including core orbitals.

TABLE II. Ionization potential (eV).

System	EXX	EXX-LDA	EXX-PBE	LDA	PBE	Expt.
H_2	16.2	17.5	17.0	10.3	10.4	15.5
OH	15.0	16.3	15.8	8.2	8.0	13.0
FH	17.4	18.9	18.4	9.8	9.6	16.0
Li_2	5.1	6.0	5.8	3.2	3.2	5.0
CO	14.1	15.6	15.1	9.1	9.1	14.0
N_2	15.5	16.9	16.4	10.4	10.3	15.6
O_2	13.6	14.8	14.3	6.9	6.8	12.1
F_2	14.5	15.9	15.4	9.7	9.5	15.7
NH_3	11.6	13.0	12.5	6.3	6.2	10.2
H_2O	13.7	15.1	14.6	7.4	7.2	12.6
CH_4	14.1	15.4	15.0	9.5	9.5	12.6
Error[a]	1.01	2.10	1.69	4.68	4.77	-

[a] Mean absolute deviation.

employing exact exchange (EXX, EXX-LDA, EXX-PBE) deviate stronger from experimental values [18,20] than the corresponding PBE results. This shows that the PBE approximation (and, even more, the LDA) describes correlation alone only quite poorly. The success of the PBE approximation and, presumably, also of other generalized gradient approximations thus relies heavily on error cancellations between exchange and correlation, quantities of different order in the electron-electron interaction. This obviously is unsatisfying, in particular, because these error cancellations probably have at least some system dependence. The dependence on such error cancellations can be avoided by starting from an exact treatment of exchange and by then concentrating on approximations for correlation alone. With the present work such a systematic development has become possible.

Energies calculated with the present EXX method agree well (within 10 kcal) with corresponding data obtained in Refs. [12,13] with the Krieger-Li-Iafrate approximation [11] for the exchange potential.

An immediate improvement of the EXX approach over conventional KS methods and over HF methods is demonstrated by the KS eigenvalues of the HOMOs listed in Table II and by the eigenvalue spectra of carbon monoxide (CO) in Fig. 1 (the findings in Fig. 1 are representative of all investigated molecules, not just for CO). The negatives of the KS eigenvalues of the HOMOs from the EXX methods, in contrast to those from conventional KS methods, are close to the corresponding ionization energies, reflecting the fact that the negative of the exact KS eigenvalue of a HOMO equals the corresponding ionization energy. Note, however, that EXX KS eigenvalues in contrast to EXX total energies are very sensitive (shifts of $\sim$1 eV are possible) with respect to the relative size of auxiliary and orbital basis sets even if both basis sets are very large, as in this work. The EXX eigenvalue spectra of CO, in contrast to those from conventional KS and the HF methods, has a physically meaningful form. Not only does the eigenvalue of the HOMO lie in the correct energetic region, but the spectrum also exhibits a Rydberg series indicated by a thick bar in Fig. 1. The use of KS orbitals and eigenvalues from the EXX method in time-dependent DFT approaches therefore seems to be promising.

The introduced method represents a procedure to generate the functional derivative of an orbital-dependent quantity, here the exchange energy, with respect to the electron density. If the method is applied not to the exchange energy but to an approximate orbital-dependent functional for the correlation energy, then the consistent *local* correlation potential is obtained.

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