Proper Treatment of Symmetries and Excited States in a Computationally Tractable Kohn-Sham Method

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A new Kohn-Sham (KS) formalism, the symmetrized generalized adiabatic connection KS formalism, is introduced. It is applicable to ground as well as excited states and does not suffer from the symmetry problems of the standard KS approach. In all cases a totally symmetric, non-spin-polarized KS Hamiltonian operator arises. Complete electronic spectra, including multiplet splittings, Rydberg series, and x-ray and Auger data can be described. Results for the carbon atom and the carbon monoxide molecule are presented.

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The treatment of symmetries in open-shell atoms or molecules is a fundamental problem in the Kohn-Sham (KS) as well as in the Hartree-Fock (HF) method [1,2]. In both methods the symmetry of an open-shell system is broken, in general. This results in a KS or HF Hamiltonian operator which has a lower symmetry than the real Hamiltonian operator of the open-shell atom or molecule. The latter Hamiltonian operator is always rotationally symmetric in spin space if relativistic effects (spin-orbit coupling) are neglected and its symmetry in ordinary space is given by the point group symmetry of the nuclei if the Born-Oppenheimer approximation is made and no external fields are present. On the other hand, the KS or HF Hamiltonian operator, in general, is spin polarized, i.e., violates rotational symmetry in spin space, and furthermore may exhibit only a reduced symmetry in ordinary space.

This leads to the highly unsatisfying situation that three electronic systems are associated with an open-shell atom or molecule: (i) the real one, (ii) an often unclearly defined model system used for the characterization and interpretation of the electronic structure, and (iii) the KS or the HF model system which is actually calculated. As an example, the carbon atom shall be considered. Its energetically lowest states are the ^3P, the ^1D, and the ^1S state of the configuration $(1s^2, 2s^2, 2p^2)$. In order to define the configuration one invokes an independent particle model system with one set of hydrogenlike orbitals with well-defined angular quantum numbers. A KS or HF calculation for the ^3P state, the carbon ground state, yields two different sets of spin-up and spin-down orbitals which furthermore, due to symmetry breaking in ordinary space, belong to the point group D_h^∞ and no longer to the full rotational group. Thus the KS or HF orbitals cannot be used to define the electronic configuration of the carbon ground state and do not yield many-electron wave functions with the proper symmetry.

In the KS formalism further problems arise. According to a commonly adopted point of view the KS formalism can be applied to the energetically lowest state of each symmetry [3]. To that end KS wave functions with symmetries belonging to the full symmetry group of the atom or molecule are required. However, in general, for an atom or molecule, the energetically lowest states of each symmetry are open shell states and thus, as just pointed out, KS orbitals and wave functions do not belong to the full symmetry group and therefore do not lead to KS wave functions of the required symmetry. Even if this point is ignored it is not possible to distinguish in conventional KS calculations states whose spin density has the same form in terms of KS orbitals, like, e.g., the $^1\Sigma_u^+$ state and the $^3\Sigma_u^+$ state with magnetic spin quantum number zero of the $(1\sigma_g^{+1}, 1\sigma_u^{+1})$ configuration of the hydrogen molecule. Thus a proper treatment of states which are the energetically lowest of their symmetry but not the ground state has, up to now, not been possible and one has to resort to approximate schemes [1] in these cases.

These problems are avoided in a symmetrized KS formalism introduced some time ago [4]. In this symmetrized KS formalism the basic quantity is no longer the electron density or the spin density, but the totally symmetric part of the spin density which is rotationally invariant in spin space and totally symmetric with respect to the symmetry in ordinary space. The totally symmetric part $\overline{\rho}$ of an arbitrary spin density $\boldsymbol{\rho}$ is obtained by applying all symmetry operations on it and by then averaging over the results. If a spin density belongs to a state with a well-defined symmetry characterized by the symmetry labels Γ, γ (Γ denotes the irreducible representation, γ labels the symmetry partners in a higher dimensional representation) its totally symmetric part is independent of γ and can alternatively be obtained by averaging over the spin densities of the symmetry partners of the state [4].

In the symmetrized KS formalism all quantities are functionals not of the electron density or spin density but of their totally symmetric part. The KS Hamiltonian operator in the symmetrized formalism always exhibits the full symmetry of the system. However, because so far approximations for the required symmetry-dependent exchange-correlation functionals have not been available it has not yet been possible to apply the symmetrized KS formalism in practice [5,6].

The problem of a proper handling of symmetry also occurs if higher excited open-shell states of an atom or molecule are considered. Recently, a generalized adiabatic connection KS (GAC-KS) formalism for the self-consistent KS treatment of excited states was introduced [7]. The GAC-KS formalism is no longer based on the Hohenberg-Kohn theorem but on generalized adiabatic connections associating a KS state with each state of the real system. Because of the problem of a proper treatment of symmetries the GAC-KS formalism so far could be applied only to a few atomic test cases [7].

In this Letter, first, the symmetrized KS formalism of Ref. [4] and the GAC-KS formalism of Ref. [7] are combined to a symmetrized GAC-KS formalism. Then it is demonstrated how the required potentials and energies can be determined. This results in a *generally applicable KS method without symmetry problems,* i.e., a KS method which can be applied to *any bound ground or excited state* of an atom or molecule and which leads in all cases to *non-spin-polarized KS Hamiltonian operators exhibiting the full symmetry* of the considered system. As an example, excited states of the carbon atom and the carbon monoxide molecule are considered.

For a start, *symmetrized* $\overline{\rho}$*-stationary wave functions* $\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]$ are defined by the generalized constrained search

$$\operatorname*{stat}_{\nu,\Psi^{\Gamma,\gamma}\to\overline{\rho}} \langle\Psi^{\Gamma,\gamma}|\hat{T} + \alpha\hat{V}_{ee}|\Psi^{\Gamma,\gamma}\rangle \rightarrow \Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]. \quad (1)$$

By $\hat{T}$ and $\hat{V}_{ee}$ the operators of the kinetic energy and the electron-electron interaction are denoted, respectively; α designates a coupling constant with values between zero and one. The $\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]$ are those wave functions of symmetry (Γ,γ) which yield a spin density with totally symmetric part $\overline{\rho}$ and for which, additionally, the expectation value $\langle\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]|\hat{T} + \alpha\hat{V}_{ee}|\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]\rangle$ is stationary with respect to variations $\delta_{\Psi^{\Gamma,\gamma}\to\overline{\rho}}$ which leave $\overline{\rho}$ unchanged. The parameter ν labels all existing wave functions $\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]$ for a given $\overline{\rho}$ in some arbitrary order. The symmetrized $\overline{\rho}$-stationary wave functions $\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha]$ with α values varying from zero to one form the generalized adiabatic connection (GAC) ν. The wave function $\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,\alpha = 0]$ shall be designated as KS wave function $\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]$. By

$$T_s^{\Gamma}[\overline{\rho},\nu] = \langle\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]|\hat{T}|\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]\rangle, \quad (2)$$

$$U[\overline{\rho}] = \int d\mathbf{r}\, d\mathbf{r}'\, \frac{\overline{\rho}(\mathbf{r})\overline{\rho}(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (3)$$

$$E_x^{\Gamma}[\overline{\rho},\nu] = \langle\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]|\hat{V}_{ee}|\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]\rangle - U[\overline{\rho}], \quad (4)$$

$$\begin{aligned} E_c^{\Gamma}[\overline{\rho},\nu] = {} & \langle\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,1]|\hat{T} + \hat{V}_{ee}|\Psi^{\Gamma,\gamma}[\overline{\rho},\nu,1]\rangle \\ & - \langle\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]|\hat{T} + \hat{V}_{ee}|\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]\rangle, \quad (5) \end{aligned}$$

functionals of $\overline{\rho}$ for the noninteracting kinetic, the Coulomb [8], the exchange [8], and the correlation energy, respectively, shall be defined. Note that the energy functionals do not depend on γ because the defining expectation values are identical for wave functions differing only by the value of γ. Because for a given symmetry (Γ,γ) there exists a one-to-one relation between the variables $\overline{\rho},\nu$ and the KS wave functions $\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]$ the latter can be used as variables instead of the former in order to represent energies by *state-dependent* functionals $T_s[\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]] = T_s^{\Gamma}[\overline{\rho},\nu]$, $E_x[\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]] = E_x^{\Gamma}[\overline{\rho},\nu]$, and $E_c[\Phi^{\Gamma,\gamma}[\overline{\rho},\nu]] = E_c^{\Gamma}[\overline{\rho},\nu]$ which exhibit an explicit dependence on KS states and only implicitly depend on $\overline{\rho}$ and ν.

From a generalization of the arguments of Ref. [7] it follows that each eigenstate $\Psi_i^{\Gamma,\gamma}$ of a given real electron system is a symmetrized $\overline{\rho}$-stationary wave function $\Psi^{\Gamma,\gamma}[\overline{\rho}_i,\nu,\alpha = 1]$ with a KS state $\Phi_j^{\Gamma,\gamma} = \Psi^{\Gamma,\gamma}[\overline{\rho}_j = \overline{\rho}_i,\nu,\alpha = 0]$ associated to it via the GAC ν. Here, $\overline{\rho}_i = \overline{\rho}_j$ is the totally symmetric part of the spin densities of $\Psi_i^{\Gamma,\gamma}$ and, by definition, also of $\Phi_j^{\Gamma,\gamma}$. Each KS state $\Phi_j^{\Gamma,\gamma}$ is the jth eigenstate of a KS equation

$$[\hat{T} + \hat{v}_s[\Gamma,\overline{\rho}_j,\nu]]\Phi_j^{\Gamma,\gamma} = E_{s,j}\Phi_j^{\Gamma,\gamma}, \quad (6)$$

$$\begin{aligned} \hat{v}_s[\Gamma,\overline{\rho}_j,\nu] = {} & \hat{v} + \hat{u}[\overline{\rho}_j] + \hat{v}_x[\Gamma,\overline{\rho}_j,\nu] \\ & + \hat{v}_c[\Gamma,\overline{\rho}_j,\nu]. \quad (7) \end{aligned}$$

In Eqs. (6) and (7) $\hat{v}_s[\Gamma,\overline{\rho}_j,\nu]$ denotes the operator corresponding to the KS potential $v_s([\Gamma,\overline{\rho}_j,\nu];\mathbf{r})$ and $\hat{v}$ the operator corresponding to the external potential $v(\mathbf{r})$ usually formed by the electrostatic potential of the nuclei. The Coulomb, exchange, and correlation potentials $u([\overline{\rho}_j];\mathbf{r})$, $v_x([\Gamma,\overline{\rho}_j,\nu];\mathbf{r})$, and $v_c([\Gamma,\overline{\rho}_j,\nu];\mathbf{r})$, respectively, generating the operators $\hat{u}[\overline{\rho}_j]$, $\hat{v}_x[\Gamma,\overline{\rho}_j,\nu]$, and $\hat{v}_c[\Gamma,\overline{\rho}_j,\nu]$ in Eq. (7), are given by the functional derivatives:

$$u([\overline{\rho}_j];\mathbf{r}) = \int d\mathbf{r}\, \frac{\overline{\rho}_j(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}, \quad (8)$$

$$v_x([\Gamma,\overline{\rho}_j,\nu];\mathbf{r}) = \frac{\delta E_x^{\Gamma}[\overline{\rho},\nu]}{\delta\overline{\rho}(\mathbf{r})}\bigg|_{\overline{\rho}(\mathbf{r})=\overline{\rho}_j(\mathbf{r})}, \quad (9)$$

$$v_c([\Gamma,\overline{\rho}_j,\nu];\mathbf{r}) = \frac{\delta E_c^{\Gamma}[\overline{\rho},\nu]}{\delta\overline{\rho}(\mathbf{r})}\bigg|_{\overline{\rho}(\mathbf{r})=\overline{\rho}_j(\mathbf{r})}. \quad (10)$$

Functional derivatives with respect to totally symmetric quantities, like $\overline{\rho}(\mathbf{r})$ [or $v_s(\mathbf{r})$ later on], always are totally symmetric functions of $\mathbf{r}$ if irrelevant, undefined non-totally-symmetric contributions are set to zero as in this work (see Sec. IIB of Ref. [4]). Functional derivatives with respect to $\overline{\rho}(\mathbf{r})$ are defined only up to the addition of a constant. Here this constant shall be chosen in such a way that all functional derivatives vanish for $r \longrightarrow \infty$.

In the treatment of an atom or molecule in the symmetrized GAC-KS formalism first eigenstates $\Psi_i^{\Gamma,\gamma}$ are chosen by specifying the configuration and symmetry of the corresponding KS wave functions $\Phi_j^{\Gamma,\gamma}$. Then for *each* chosen eigenstate state $\Psi_i^{\Gamma,\gamma}$ the corresponding KS equation (6) has to be solved self-consistently to obtain the associated KS wave function $\Phi_j^{\Gamma,\gamma}$ and the totally symmetric contribution $\overline{\rho}_i = \overline{\rho}_j$ of the spin density. The many-particle KS equation (6) decouples in corresponding one-particle KS equations for the KS orbitals $\phi_p^{\Lambda,\lambda}[\Gamma,\overline{\rho}_j,\nu]$ (two-dimensional spinors) building the KS wave function $\Phi_j^{\Gamma,\gamma}$ and their eigenvalues $\varepsilon_p^{\Lambda,\lambda}[\Gamma,\overline{\rho}_j,\nu]$. By (Λ,λ) the symmetry of the KS orbitals is denoted. In a second step then the energy E_i^{Γ} of the state $\Psi_i^{\Gamma,\gamma}$ is obtained as a sum of the corresponding state-dependent energy functionals $E_i^{\Gamma} = T_s[\Phi_j^{\Gamma,\gamma}] + U[\overline{\rho}_j] + E_x[\Phi_j^{\Gamma,\gamma}] + E_c[\Phi_j^{\Gamma,\gamma}] + \int d\mathbf{r}\, v(\mathbf{r})\overline{\rho}_j(\mathbf{r})$.

Having established the symmetrized GAC-KS formalism the remaining task is to devise a method for its use in practice. This Letter introduces a basis set method which employs Gaussian- or Slater-type basis sets and is generally applicable, i.e., to arbitrary atoms and molecules. The crucial step is the evaluation of the exchange and correlation energies and potentials from state-dependent functionals $E_x[\Phi_j^{\Gamma,\gamma}]$ and $E_c[\Phi_j^{\Gamma,\gamma}]$. The handling of state-dependent functionals in the symmetrized GAC-KS formalism is demonstrated by treating the exchange energy and potential exactly. However, the approach also can be applied to (approximate) state-dependent correlation functionals. Because, at present, such state-dependent correlation functionals are not available, correlation is, in this work, either neglected (exact exchange-only approach labeled EXX) or treated by substituting $\overline{\rho}_j(\mathbf{r})$ into approximate correlation functionals from the standard KS formalism. In the approach labeled EXX-LDA the local density approximation [9] for correlation is used, and in the approach labeled EXX-PBE (Perdew-Burke-Ernzerhof) the correlation functional according to Ref. [10].

In order to represent the energy $E_i^{\Gamma,\gamma}$ in terms of the KS orbitals $\phi_p^{\Lambda,\lambda}[\Gamma,\overline{\rho}_j,\nu]$ (for notational simplicity, the argument $[\Gamma,\overline{\rho}_j,\nu]$ will be suppressed from now on), the average density matrix $\overline{\rho}_j(\mathbf{r},\mathbf{r}')$ is defined by

$$\overline{\rho}_j(\mathbf{r},\mathbf{r}') = \sum_{\Lambda,\lambda,p} f_j(\Lambda,p)\phi_p^{\Lambda,\lambda}(\mathbf{r})\phi_p^{\Lambda,\lambda\dagger}(\mathbf{r}'). \tag{11}$$

In Eq. (11), $f_j(\Lambda,p)$ is the average fractional occupation of the KS orbitals according to the configuration. The average density matrix then yields $\overline{\rho}_j(\mathbf{r}) = \overline{\rho}_j(\mathbf{r},\mathbf{r})$, which subsequently yields the Coulomb energy $U[\overline{\rho}_j]$ via Eq. (3), the energy contribution $\int d\mathbf{r}\, v(\mathbf{r})\overline{\rho}_j(\mathbf{r})$, and, in the EXX-LDA and EXX-PBE procedures, the approximate correlation energy. The noninteracting kinetic energy is given by $T_s[\Phi_j^{\Gamma,\gamma}] = \sum_{\Lambda,\lambda,p} f_j(\Lambda,p)\langle\phi_p^{\Lambda,\lambda}|\hat{T}|\phi_p^{\Lambda,\lambda}\rangle$ in terms of the KS orbitals.

For the exchange energy, orbital-dependent expressions result from evaluating Eqs. (4). In the example of the carbon atom the following energy quantities are defined:

$$Y(\text{conf.}) = \frac{1}{2}\int d\mathbf{r}\, d\mathbf{r}' \times \frac{\overline{\rho}_j(\mathbf{r},\mathbf{r}')\overline{\rho}_j(\mathbf{r}',\mathbf{r})}{|\mathbf{r}-\mathbf{r}'|},$$

$$U(p,q) = \frac{1}{2}\sum_{\lambda,\lambda'}\int d\mathbf{r}\, d\mathbf{r}' \times \frac{\phi_p^{\Lambda,\lambda\dagger}(\mathbf{r})\phi_p^{\Lambda,\lambda}(\mathbf{r})\phi_q^{\Lambda',\lambda'\dagger}(\mathbf{r}')\phi_q^{\Lambda',\lambda'}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|},$$

$$Y(p,q) = \frac{1}{2}\sum_{\lambda,\lambda'}\int d\mathbf{r}\, d\mathbf{r}' \times \frac{\phi_p^{\Lambda,\lambda\dagger}(\mathbf{r})\phi_q^{\Lambda',\lambda'}(\mathbf{r})\phi_q^{\Lambda',\lambda'\dagger}(\mathbf{r}')\phi_p^{\Lambda,\lambda}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}.$$

For the carbon ^3P, ^1D, and ^1S states of the configuration $(1s^2,2s^2,2p^2)$ the exchange energy is given by $Y(1s^2,2s^2,2p^2) - (1/36)U(2p,2p) - (1/18)Y(2p,2p)$, $Y(1s^2,2s^2,2p^2) - (11/180)U(2p,2p) + (13/90)Y(2p,2p)$, and $Y(1s^2,2s^2,2p^2) - (1/9)U(2p,2p) + (4/9)\times Y(2p,2p)$, respectively [11].

The Coulomb potential is given by Eq. (8), and the LDA or PBE correlation potentials by simply substituting $\overline{\rho}_j(\mathbf{r})$ in the corresponding functionals for the correlation potential. For the exchange potential, the EXX equation

$$\int d\mathbf{r}'\, \overline{X}_s(\mathbf{r},\mathbf{r}')v_x([\Gamma,\overline{\rho}_j,\nu];\mathbf{r}') = \frac{\delta E_x[\Phi_j^{\Gamma,\gamma}]}{\delta v_s(\mathbf{r})} \tag{12}$$

can be derived by generalizing the arguments of Ref. [12]. The response function $\overline{X}_s$ of the KS system describing changes of the totally symmetric part of the spin density of $\Phi_j^{\Gamma,\gamma}$ due to changes of the KS potential v_s is given by perturbation theory in terms of the KS orbitals. The functional derviative $\delta E_x[\Phi_j^{\Gamma,\gamma}]/\delta v_s(\mathbf{r})$ on the right-hand side of Eq. (12) is accessible because $E_x[\Phi_j^{\Gamma,\gamma}]$ is known in terms of the KS orbitals and the functional derivative of the KS orbitals with respect to $v_s(\mathbf{r})$ is again given by perturbation theory.

In order to solve the EXX equation (12), following Ref. [12], an exchange charge density $\rho_x(\mathbf{r}) = (-1/4\pi)\nabla^2 v_x(\mathbf{r})$ is introduced. It yields the exchange potential according to $v_x(\mathbf{r}) = \int d\mathbf{r}'\, \rho_x(\mathbf{r}')/|\mathbf{r}-\mathbf{r}'|$ [12,13]. If the latter expression for $v_x(\mathbf{r})$ is inserted into Eq. (12), then an EXX equation for $\rho_x(\mathbf{r})$ emerges. The exchange charge density $\rho_x(\mathbf{r})$ and its EXX equation is then expanded in an auxiliary basis set of Slater- or Gaussian-type functions which is required in addition to the basis set for the representation of the KS orbitals. The EXX equation for $\rho_x(\mathbf{r})$ then turns into a matrix equation for the expansion coefficients $\rho_x(\mathbf{r})$. In this work large uncontracted Gaussian basis sets are employed. The occurring matrix elements are calculated with the programs PARAGAUSS [14] and GAMESS [15].

For carbon the configurations $(1s^2,2s^2,2p^2)$ with states ^3P, ^1D, and ^1S, $(1s^2,2s^1,2p^3)$ with states ^5S,

TABLE I. Carbon excitation energies (eV).

Config.	Sym.	EXX	EXX-LDA	EXX-PBE	Expt.[a]
$2s^2,2p^2$	^1D	1.54	1.57	1.57	1.26
$2s^2,2p^2$	^1S	3.76	3.85	3.85	2.68
$2s^1,2p^3$	^5S	2.42	2.40	2.47	4.18
$2s^1,2p^3$	^3D	7.98	8.05	8.10	7.94
$2s^1,2p^3$	^3P	9.53	9.63	9.67	9.33
$2s^2,2p^1,3s^1$	^3P	7.27	7.96	7.81	7.48
$2s^2,2p^1,3s^1$	^1P	7.49	8.20	8.02	7.68
$2s^2,2p^1,4s^1$	^3P	9.25	10.19	9.94	9.68
$2s^2,2p^1,4s^1$	^1P	9.31	10.26	10.00	9.71
$2s^2,2p^1,5s^1$	^3P	9.92	10.99	10.67	10.38
$2s^2,2p^1,5s^1$	^1P	9.94	11.01	10.69	10.40
$2s^2,2p^1,6s^1$	^3P	10.23	11.41	11.04	10.70
$2s^2,2p^1,6s^1$	^1P	10.24	11.43	11.05	10.71
$2s^2,2p^1,7s^1$	^3P	10.39	11.67	11.23	10.87
$2s^2,2p^1,7s^1$	^1P	10.40	11.67	11.24	10.88

[a]See Ref. [16].

TABLE II. CO excitation energies (eV).

Config.	Sym.	EXX	EXX-LDA	EXX-PBE	Expt.[a]
$1\pi^4,5\sigma^1,2\pi^1$	$^3\Pi$	5.90	5.91	5.86	6.32
$1\pi^4,5\sigma^1,2\pi^1$	$^1\Pi$	8.98	9.06	9.01	8.51
$1\pi^3,5\sigma^2,2\pi^1$	$^3\Sigma^+$	7.07	7.12	7.21	8.51
$1\pi^3,5\sigma^2,2\pi^1$	$^3\Delta$	7.80	7.85	7.95	9.36
$1\pi^3,5\sigma^2,2\pi^1$	$^3\Sigma^-$	8.49	8.55	8.65	9.88
$1\pi^3,5\sigma^2,2\pi^1$	$^1\Sigma^-$	8.49	8.55	8.65	9.88
$1\pi^3,5\sigma^2,2\pi^1$	$^1\Delta$	8.77	8.82	8.93	10.23

[a]See Ref. [17].

^3D, and ^3P, and the Rydberg series of configuration $(1s^2,2s^2,2p^1,ns^1)$ for $3 \leq n \leq 7$ with states of symmetry ^3P and ^1P are considered. Carbon monoxide (CO) belongs to the point group $C_{\infty v}$; the involved KS orbitals either belong to the irreducible representation Σ^+ (σ orbitals) or Π (π orbitals, twofold degenerate with respect to symmetry in ordinary space). Here the configuration $(1\sigma^2,2\sigma^2,3\sigma^2,4\sigma^2,1\pi^4,5\sigma^2)$ leading to the $^1\Sigma^+$ ground state and the configurations $(1\sigma^2,2\sigma^2,3\sigma^2,4\sigma^2,1\pi^4,5\sigma^1,2\pi^1)$ with states $^3\Pi$ and $^1\Pi$ and $(1\sigma^2,2\sigma^2,3\sigma^2,4\sigma^2,1\pi^3,5\sigma^2,2\pi^1)$ with states $^3\Sigma^+$, $^3\Delta$, $^3\Sigma^-$, $^1\Sigma^-$, and $^1\Delta$ are treated.

The EXX exitation energies for carbon listed in Table I agree within a few tenths of an eV with the experimental values. Exceptions are the excitations into the $(1s^2,2s^2,2p^2)$ ^1S and $(1s^2,2s^1,2p^3)$ ^5S states. In Table II excitation energies for CO (bond distance 1.128 Å) are displayed. Excitations into the two states of configuration $(1\sigma^2,2\sigma^2,3\sigma^2,4\sigma^2,1\pi^4,5\sigma^1,2\pi^1)$ are quite well described by the GAC-KS methods. EXX excitation energies for the states of configuration $(1\sigma^2,2\sigma^2,3\sigma^2,4\sigma^2,1\pi^4,5\sigma^1,2\pi^1)$ are consistently too low by ~1.5 eV; the corresponding multiplet splitting, however, is obtained with a good accuracy of ~0.1 eV. The deviations between EXX and experimental data have to be attributed to correlation effects which are neglected in the exchange-only EXX approach. The inclusion of correlation on the LDA or PBE level does not lead to systematic improvements because the employed LDA and PBE functionals (i) are not state dependent and not designed for excited states and (ii) rely on error cancellations with approximate exchange functionals which are not present if exchange is treated exactly [12].

By calculating highly excited states with core holes, data describing x-ray or Auger spectroscopy can be obtained with the symmetrized GAC-KS approach. For example, the EXX binding energy of the carbon $1s$ electron calculated as the difference between the energies of the $(1s^1,2s^2,2p^2)$ ^4P and $(1s^2,2s^2,2p^2)$ ^3P states with 295.2 eV excellently agrees with the experimental value of 296.9 eV [18].

More important than the details of the comparison of the calculated to the experimental excitation energies is the demonstration that the symmetrized GAC-KS formalism is applicable in practice to a wide range of atomic and molecular states, including highly excited Rydberg states and states with core holes.

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