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Local-density-functional approximation for exchange-correlation potential*

Application of the self-consistent and statistical exchange-correlation parameters to the calculation of the electron binding energies

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Local exchange-correlation potential has been derived starting from the free-electron gas model. *Ab initio* way of calculating the parameter α of the Xα method is presented. Self-consistent and statistical exchange-correlation parameters have been determined. The self-consistent parameters α have been used to calculate the electron binding energies of Neon, Argon and Krypton. We suggest using statistical exchange-correlation parameter in molecular calculations. The statistical exchange-correlation parameter has been applied to study the electron binding energies of the molecules H_2O and HF. It is shown that the electron binding energies calculated with the self-consistent and the statistical parameters α show agreement with the experimental values.

Key words: Local density approximation — Xα method — *Ab initio* SCF parameters α — *Ab initio* statistical parameters α — Electron binding energies — Transition state method

Introduction

The density functional theory makes it possible to solve the many-body problem exactly. According to the Hohenberg–Kohn theorem [1] the total energy of a system can be expressed as the functional of the electron density. Unfortunately, the exact exchange-correlation energy density and potential are not known. One of the most widely used approximation in the density functional theory is the local density approximation. Several approximate local exchange-correlation

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* Dedicated to Professor J. Koutecký on the occasion of his 65th birthday

potentials are applied in the frame of the local density approximation (see e.g. [2]). Here an *ab initio* self-consistent exchange potential is presented.

The simplest form of local density approximation is the so-called Xα method. Ever since the appearance of the Xα method [3] the way of choosing the value of α has been a fundamental problem of the method. Usually the parameters α determined by Schwarz [4] are used (Schwarz calculated parameters α_{HF} so that the total Xα energy be equal to the Hartree-Fock total energy). Gopinathan, Whitehead and Bogdanovic [5] derived the exchange parameter of the Xα method assuming a linear variation of the Fermi-hole density. Nevertheless, they adjusted their theoretical values α_{ta} so that the limiting value of α_{ta} for large atomic numbers be equal to the limiting value of α_{HF}.

In a previous paper [6] one of the authors presented a new theoretical method that makes it possible to determine self-consistent parameters α. As the parameters α have been determined in an *ab initio* way, the Xα method containing this parameter can be regarded an *ab initio* one.

It is also possible to define the so-called statistical exchange-correlation parameter [7]. We believe that the statistical parameter can be especially useful in molecular calculations as its application will not lead to any increase in computer time.

In order to test the self-consistent and statistical exchange-correlation parameters the electron binding energies have been studied in a few atoms and molecules.

The self-consistant parameters α have been used to calculate the electron binding energies of Ne, Ar and Kr (the binding energy of an electron is defined as the energy which is needed to remove the electron from the atom). It is pointed out that the SCF parameters α provide electron binding energies close to the experimental ones.

The electron binding energies of the molecules H_2O and HF have been studied. It seems that the statistical exchange-correlation parameter can be effectively applied in molecular Xα calculations.

Self-consistent exchange-correlation potentials

The self-consistent and the statistical parameters α

The starting point of the derivation of the new exchange potential is the free-electron gas model [8]. The exchange potential for the electrons with spin up is

$$V_{X\uparrow}(1) = -8F(\eta)\left(\frac{3}{4\pi}\rho_\uparrow(1)\right)^{1/3}, \tag{1}$$

where

$$F(\eta) = \frac{1}{2} + \frac{1-\eta^2}{4\eta}\ln\left|\frac{1+\eta}{1-\eta}\right| \tag{2}$$

and $\rho_\uparrow$ is the total electron density of the electrons having spin up. $\eta=|\vec{k}|/|\vec{k}_F|$ in the reduced momentum of the electron and $E_{F\uparrow}=k_{F\uparrow}^2=(6\pi\rho_\uparrow)^{1/3}$ is the Fermi energy. Averaging in the momentum space

$$V_{X\uparrow}(1)=-8\left(\frac{3}{4\pi}\rho_\uparrow(1)\right)^{1/3}\frac{\displaystyle\int_{\eta_1}^{\eta_2}F(\eta)\eta^2\,d\eta}{\displaystyle\int_{\eta_1}^{\eta_2}\eta^2\,d\eta} \tag{3}$$

we get the Xα exchange-correlation with the parameter

$$\alpha=\left\{\frac{1}{2}(\eta^3+\eta)-\frac{1}{4}(\eta^2-1)^2\ln\left|\frac{1+\eta}{1-\eta}\right|\right\}_{\eta_1}^{\eta_2}(\{\eta^3\}_{\eta_1}^{\eta_2})^{-1}. \tag{4}$$

Averaging over all the occupied states, that is $\eta_1=0$ and $\eta_2=1$, we obtain α suggested by Slater [3]. If the averaging procedure is carried out over a thin shell near k_F, that is, $\eta_1=k_{F\uparrow}-\varepsilon/k_{F\uparrow}$, $\eta_2=1$ with $\varepsilon\to 0$ we get $\alpha=\frac{2}{3}$. This is the parameter α that was first proposed by one of the authors [9]. Certainly, the averaging procedure is done for a too large space in the first case and a too small in the second case. Between these extreme cases it is possible to introduce a new parameter α by the following process. On averaging over a thin shell near Fermi surface for a layer containing $\nu_\uparrow$ electrons in the unit volume, that is,

$$\eta_1=\eta=\left(1-\frac{\nu_\uparrow}{\rho_\uparrow}\right)^{1/3},\qquad \eta_2=1,$$

we obtain

$$\alpha_{\text{shell}}(1)=\frac{\rho_\uparrow}{\nu_\uparrow}\left\{1-\tfrac{1}{2}\eta^3-\tfrac{1}{2}\eta+\tfrac{1}{4}(\eta^2-1)^2\ln\left|\frac{1+\eta}{1-\eta}\right|\right\}, \tag{5}$$

where

$$\nu_\uparrow(1)=u_i^*(1)u_i(1) \tag{6}$$

is the density of the electron considered. The parameter and therefore the exchange-correlation potential is the same for electrons with the same spin orbitals, i.e. for the same shell, but it is different for different shells. An analysis of the r-dependence of the parameters for different shells can be found in [10]. Denoting by α_{shell}^j the parameter α for shell j, with another averaging process we get

$$\alpha_\uparrow(1)=\frac{\sum_{j\uparrow}n_j\alpha_{\text{shell}}^j}{\sum_{j\uparrow}n_j}, \tag{7}$$

where n_j is the number of electrons in the shell j. By this procedure the same exchange-correlation potential is gained for the electrons with the same spin

$$V_{X\alpha_\uparrow(1)}(1)=-6\alpha(1)\left(\frac{3}{4\pi}\rho_\uparrow(1)\right)^{1/3}. \tag{8}$$

Nevertheless $\alpha_\uparrow(1)$ is not a constant as it is usual in the Xα method but a function of the position (1). In order to compare our new potential (8) to the usual Xα exchange-correlation potential

$$V_{X\alpha_\uparrow}(1) = -6\alpha_\uparrow\left(\frac{3}{4\pi}\rho_\uparrow(1)\right)^{1/3} \tag{9}$$

we can take a constant parameter α so that the mean squared deviation of $V_{X\alpha\uparrow}(1)$ and $V_{X\alpha\uparrow(1)}(1)$ be a minimum. It can be pointed out [7] that the function $\alpha(1)$ only slightly depends on the position vector $\boldsymbol{r}$, there are only small deviations from a constant value. This fact makes it very plausible to introduce a constant α value.

This $\alpha_\uparrow$ can be determined self-consistently. Starting from an initial parameter α and exchange-correlation potential it is possible to solve the Xα one-electron equations

$$\left\{-\Delta_1 - \frac{2Z}{r_1} + 2\int\frac{\rho(2)}{12}\,dv_2 - 6\alpha_\uparrow\left(\frac{3}{4\pi}\rho_\uparrow(1)\right)^{1/3}\right\}u_{i\uparrow}(1) = \varepsilon_{i\uparrow}u_{i\uparrow}(1), \tag{10}$$

where Δ is the Laplacian, Z is the atomic number, $\varepsilon_{i\uparrow}$ are the Xα one-electron energies, $u_{i\uparrow}$ are the spin orbitals

$$\rho(1) = \rho_\uparrow(1) + \rho_\downarrow(1) \tag{11}$$

is the total electron density. From the determined spin orbitals and electron density we can calculate the new parameter α and potential using the expressions (5)-(9). With the new exchange-correlation potential the Xα one-electron equations are solved again. This procedure has to be carried on until self-consistency is attained.

It is worthwhile mentioning that the Xα one-electron equations (10) can be solved with the potential (8), too, i.e. with a non-constant function $\alpha_\uparrow(1)$. Moreover one can use different exchange-correlation potentials for different spin orbitals, i.e. different $\alpha^{j}_{\text{shell}}(1)$ for different shells using the expression (5).

The main advantage of applying a constant parameter α in the exchange-correlation potential is its simplicity. Further this constant parameter α is determined in an *ab initio* self-consistent way and is denoted by α_{SCF}.

The method presented here is a generalization of that of Slater and Gáspár-Kohn-Sham, as it contains those as special cases.

It is a self-contained method as there is no need of any external to the method, parameter. The exchange-correlation potentials defined above can also be given without any reference to the parameter α. We separated a factor α from the exchange-correlation potential (8) only to compare it with the parameter α of the original Xα method. The exchange-correlation potential (8) depends only on the total electron density and the one-electron densities, there is no adjustable parameter in it. The parameter α can be determined using the one-electron and the total electron densities (Eqs. (5)-(7)), without any adjustment.

This new way of calculating self-consistent parameters can also be applied to molecules and solids.

It is possible to introduce another parameter α, the so-called statistical exchange-correlation parameter α_{stat} [7]. In the free-electron gas model

$$\frac{\nu_{i\uparrow}}{\rho_\uparrow}=\frac{1}{n_\uparrow}, \tag{12}$$

where $n_\uparrow$ is the number of electrons having spin up. Using expression (12) in η, i.e.

$$\eta_\uparrow=\left(1-\frac{1}{n_\uparrow}\right)^{1/3}, \tag{13}$$

and putting it into expression (5), the statistical exchange-correlation parameter

$$\alpha_{\uparrow\text{stat}}=\tfrac{1}{2}n_\uparrow\left\{\frac{1}{n_\uparrow}+(1-\eta_\uparrow)+\tfrac{1}{4}(\eta_\uparrow^2-1)^2\ln\left|\frac{1+\eta_\uparrow}{1-\eta_\uparrow}\right|\right\} \tag{14}$$

is defined. The parameter α_{stat} depends only on the number of electrons.

It has been shown [7] that the self-consistent and the statistical exchange-correlation parameters differ only in second or higher order terms.

As it will be pointed out below the application of the statistical exchange-correlation parameter is especially useful in molecular calculations.

Electron binding energies of atoms calculated by the self-consistent exchange-correlation parameter

The way of calculating the ionization energies and the electron binding energies in the Xα method is the transition state method. According to Slater's transition state concept [11] the ionization energy is simple the negative of the Xα eigenvalue $\varepsilon_{iX\alpha}$ with the occupation number $n_i=n_{i0}-\frac{1}{2}$ for the ith orbital

$$I_i=-\varepsilon_{iX\alpha}(n_{i0}-\tfrac{1}{2}). \tag{15}$$

As a generalization of Slater's transition state method Williams, de Groot and Sommers [12] derived slightly more accurate ionization energies

$$I_i=-\tfrac{1}{4}\varepsilon_{iX\alpha}(n_i=1)-\tfrac{1}{4}\varepsilon_{iX\alpha}(n_i=\tfrac{1}{3}). \tag{16}$$

Tables 1–3 present the electron binding energies for Ne, Ar and Kr atoms. We calculated the electron binding energies with the expression (15) for the parameters α_{HF}, α_{SCF} and with the expression (16) for the parameter α_{SCF} (energies are in Rydbergs). There is only a slight difference between the electron binding energies calculated using the expressions (15) and (16). So there is no need of applying the more complicated formula (16) to determine the ionization energies. Tables 1–3 include the experimental results and the Hartree–Fock values, too. Recently Brandi, Matos and Ferreira [13] have introduced the transition state concept into the Hartree–Fock method. Tables 1 and 2 contain their results, too.

Table 1. Electron binding energies of neon atom calculated by the Xα method with α_{HF}, α_{SCF} using the expression (15) and with α_{SCF} using the expression (16), the Hartree-Fock theory using the Koopman's theorem [17], the total energy difference in the Hartree-Fock theory (ΔSCF) [17], and the transition state method [13] and experimental electron binding energies [14] subjected to the relativistic correction calculated by Herman and Skillman [16] (all energies are in Rydbergs)

	Xα Transition state calculated by Eq. (15)		Xα Transition state calculated by Eq. (16)	HF Koopmans' theorem	HF ΔSCF	HF Transition state	Exp (ESCA)	Exp (relat. corr.)
	α_{HF}	α_{SCF}	α_{SCF}					
1s	64.478	64.626	64.639	65.545	63.823	63.822	63.958	63.88
2s	3.319	3.358	3.366	3.861	3.616	3.608	3.559	3.54
2p	1.636	1.671	1.683	1.701	1.456	1.446	1.587	1.59

Table 2. The electron binding energies of argon atom calculated by the Xα method with α_{HF}, α_{SCF} using the expression (15) and with α_{SCF} using the expression (16), the Hartree-Fock theory using the Koopmans' theorem [17], the total energy difference in the Hartree-Fock theory (ΔSCF) [17], and the transition state method [13] and the experimental electron binding energies [14] subjected to the relativistic correlation calculated by Herman and Skillman [16] (all energies are in Rydbergs)

	Xα Transition state calculated by Eq. (15)		Xα Transition state calculated by Eq. (16)	HF Koopmans' theorem	HF ΔSCF	HF Transition state	Exp (ESCA)	Exp (relat. corr.)
	α_{HF}	α_{SCF}	α_{SCF}					
1s	235.618	235.532	235.532	237.222	234.838	234.802	235.627	234.88
2s	22.964	22.939	22.950	24.644	23.874	23.861	23.982	23.95
2p	18.472	18.401	18.415	19.143	18.400	18.507	18.312	18.46
3s	2.188	2.180	2.185	2.555	2.434	2.427	2.153	2.12
3p	1.139	1.133	1.138	1.182	1.085	1.137	1.162	1.16

For comparison ESCA electron binding energies [14] are also presented. Experimental results including relativistic corrections calculated by Herman and Skillman [15] are from Slater [16].

The best results for the electron binding energies are given by the Hartree-Fock ΔSCF [17] and the Hartree-Fock transition state method. The results provided by α_{SCF} and α_{HF} only slightly differ from the experimental ones. Even the Hartree-Fock values calculated with the Koopmans' theorem are not so near to the experimental ones. The results by α_{HF} are little closer to the experimental ones than ones calculated by α_{SCF}. (But there is not much difference between them.) We can conclude that the theoretical self-consistent parameters α_{SCF} provide ionization energies which are almost the same as the values determined by α_{HF} and both of them are in agreement with the experimental results. So our theoretically well-founded parameters α_{SCF} are as good in the calculation of

Table 3. The electron binding energies of krypton atom calculated by the Xα method with α_{HF}, α_{SCF} using the expression (15) and with α_{SCF} using the expression (16), the Hartree–Fock theory using the Koopmans' [17] and the experimental electron binding energies [14] subjected to the relativistic correction calculated by Herman and Skillman [16] (all energies are in Rydbergs)

	Xα Transition state calculated by Eq. (15) α_{HF}	α_{SCF}	Xα Transition state calculated by Eq. (16) α_{SCF}	HF Koopmans' theorem	Exp (ESCA)	Exp (relat. corr.)
1s	1037.081	1036.699	1036.662	1040.332	—	1033.89
2s	135.345	135.229	135.241	139.807	141.455	136.57
2p	123.428	123.302	123.317	126.019	124.645	123.78
3s	19.557	19.512	19.520	21.699	21.520	21.10
3p	15.092	15.048	15.056	16.663	15.949	15.67
3d	7.050	7.010	7.020	7.650	6.922	7.03
4s	1.993	1.979	1.983	2.306	2.014	1.87
4p	0.996	0.984	0.988	1.048	1.035	1.01

electron binding energies as the parameter α_{HF} that had been determined by an adjustment [4].

Electron binding energies of molecules calculated by the statistical exchange-correlation parameter

Atomic Xα calculations are generally done by the parameter α_{HF}. In principle, the parameter α_{HF} can also be determined for the molecules, too. In order to calculate the parameter α_{HF}, i.e. the value of α for which the total Xα energy is equal to the total Hartree–Fock energy, one has to know the total Hartree–Fock energy beforehand. However, nowadays the Hartree–Fock energy is not available for most of the molecules. This is why the atomic parameters α_{HF} are often applied even in molecular calculations. In the MS Xα method [11] generally the atomic α_{HF} are used in the so-called atomic spheres and some average of the atomic values α_{HF} is applied in the so-called outer and interatomic regions. The parameter 0.7 suggested by Baerends and Ros [18] is usually used in the DV Xα and LCAO Xα calculations. On the grounds of several molecular Xα calculations Baerends and Ros found the value of 0.7 the best for molecular calculations.

The self-consistent and statistical exchange-correlation parameters can be applied in molecular calculations, too. As the parameter α_{SCF} is determined self-consistently, its application will cause some increase in the computational time. However, one can use the statistical exchange-correlation parameter in molecular calculations without any increase in time of computation. α_{stat} depends only on the number of electrons and its value can be directly calculated by the help of the formulae (13)–(14) before carrying out the molecular calculation. Applying the statistical parameter one can also easily explain [7] why the value of 0.7 works so well for a large variety of molecules.

Table 4. Electron binding energies of the molecule H_2O (in Rydbergs)

	LCAO Xα (α_{stat})	DV Xα [19]	XαSW [20]	LCAO MO SCF [21]	Exp [14]
$1a_1$	40.472	—	40.122	41.174	39.682
$2a_1$	2.404	2.316	2.212	2.704	2.366
$1b_2$	1.462	1.396	1.154	1.420	1.352
$3a_1$	1.122	1.066	1.140	1.162	1.080
$1b_1$	1.002	0.934	1.102	1.014	0.926

Table 5. Electron binding energies of the molecule HF (in Rydbergs)

	LCAO Xα [22]	DVXα [19]	HF [23]	Exp [24]
1σ	51.8234	—	50.9561	51.0075
2σ	2.7981	2.7267	3.2016	2.9142
3σ	1.5074	1.4920	1.5361	1.4619
1π	1.2428	1.1980	1.3002	1.1848

The electron binding energies of the molecules H_2O and HF have been studied using the statistical parameter. We have chosen the LCAO Xα method for our calculations. As this method does not contain muffin-tin potential, it can be considered more appropriate for test calculations. Table 4 includes the electron binding energies of H_2O. The value of α_{stat} is 0.75783. The DVXα calculations have been done with the value of 0.7 [19], while in the MS Xα calculations different values of α have been used in the different molecular regions [20].

Table 5 contains the electron binding energies of HF. The LCAO Xα calculations have been carried out using the parameter $\alpha = 0.75729$ [22]. It is almost equal to the statistical parameter ($\alpha_{stat} = 0.75783$). The value of 0.7 has been applied in the DVXα [19] calculations.

The results presented above demonstrate that the electron binding energies can be accurately predicted by the LCAO Xα model using the statistical exchange-correlations parameter. Both the LCAO and DV Xα binding energies are in good agreement with the experiment.

Conclusion

Using *ab initio* exchange-correlation potential makes it possible to determine the parameter α of the Xα method in an *ab initio* way. So the Xα method having this parameter can be considered an *ab initio* one. Self-consistent and statistical exchange-correlation parameters have been defined. Both of them turned out to be adequate in calculating electron binding energies. As the application of the statistical parameter will not require any increase in computer time, we suggest using this parameter in molecular calculations.

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