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On the Correction of Exchange Potentials

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The statistical exchange potentials are corrected in such a way that the outer part of the atom with low electron densities, where these potentials are not valid, are excluded.

Die hier durchgeführte Korrektion der statistischen Austauschpotentiale besteht darin, daß die äußeren Gebiete der Atome, in welchen die Elektronendichte klein ist und wo diese Potentiale versagen, ausgeschlossen werden.

Les potentiels d'échange statislques sont corrigés de manière à ce que soit exclue la partie extèrne de l'atome où la densité électronique est basse et où ces potentiels ne sont pas valables.

Two kinds of statistical exchange potentials are known: one is the Slater average potential

$$V_a^m = \tfrac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} e\,\varrho^{1/3}\,,$$

which represents the average exchange interaction between one electron and the other electrons of the atom, the other is the exchange potential

$$V_a^\mu = \left(\frac{3}{\pi}\right)^{1/3} e\,\varrho^{1/3}$$

expressing the exchange interaction between the core electrons and the electrons of maximum energy (the valence electrons) in the atom [*1*, *2*, *4*, *6*], where e is the positive electric elementary charge and ϱ the electron density. These potentials give a good approximation in the interior of the atom where the electron density is high, but are not valid on the periphery where the electron density is low.

One reason for this is that statistical methods cannot be applied to low electron densities and an other reason is the following. Consider a free electron gas of N electrons contained in a volume Ω and suppose the electrons fill the lowest $n = N/2$ states (which are described by plane waves) with pairwise opposite spins. If we assume in the volume Ω a continuously distributed positive charge, the absolute value of which equals that of the electrons, then the electrostatic interaction of the electrons is compensated and the energy of the electrons consists, if we disregard the correlation, of the kinetic energy $\varkappa_k\,\varrho^{5/3}\,\Omega$ and of the exchange energy $-\varkappa_a\,\varrho^{4/3}\,\Omega$, where $\varrho = N/\Omega$ is the electron density, $\varkappa_k$ and $\varkappa_a$ are the following universal constants $\varkappa_k = 3/10(3\pi^2)^{2/3}\,e^2\,a_0$, $\varkappa_a = 3/4(3/\pi)^{1/3}\,e^2$ and a_0 denotes the first H-radius. In equilibrium the electron density takes on the finite value

$$\varrho_0 = \left(\frac{\varkappa_a}{2\,\varkappa_k}\right)^3 \tag{1}$$

which is identical with the density on the boundary of the statistical Thomas-Fermi-Dirac atom. Electron densities smaller than ϱ_0 will not occur in this neutral electron gas.

From these considerations the idea is plausible that we should disregard electron states with momenta smaller than $p_0 = \frac{1}{2}(3/\pi)^{1/3} h\, \varrho_0^{1/3}$ when summing over states (integrating according to the momentum p) in the calculation of exchange energy and exchange potentials, i.e. we should integrate from $p = p_0$ to the maximum momentum p_μ rather than from $p = 0$. We obtain in this way by a calculation similar to that of V_a^m and V_a^μ [*4*] the following result

$$V_{a\,\mathrm{corr}}^m = \frac{3}{2}\left(\frac{3}{\pi}\right)^{1/3} e\,\varrho^{1/3}\,[1 - s_m(x)] \tag{2}$$

and

$$V_{a\,\mathrm{corr}}^\mu = \left(\frac{3}{\pi}\right)^{1/3} e\,\varrho^{1/3}\,[1 - s_\mu(x)]\,, \tag{3}$$

where the corrections have the form

$$s_m(x) = x - \frac{1}{2}\,\frac{(1-x^2)^2}{1-x^3}\ln\left|\frac{1+x}{1-x}\right| \tag{4}$$

and

$$s_\mu(x) = x - \frac{1}{2}(1 - x^2)\ln\left|\frac{1+x}{1-x}\right|\,, \tag{5}$$

$$x = \frac{p_0}{p_\mu} = \left(\frac{\varrho_0}{\varrho}\right)^{1/3}. \tag{6}$$

Both corrected exchange potentials vanish at $x = 1$, i.e. at $\varrho = \varrho_0$ and must be identified with 0 at densities smaller than ϱ_0.

The corrections $s_m(x)$ and $s_\mu(x)$ are tabulated in the Table. It can be seen that these corrections are of interest only for $x > \frac{1}{2}$. As to their applications, it may be important that s_m and s_μ can be approximated by x^3 and x^4 resp. The fact that in the region $0 < x < \frac{1}{2}$ these approximations are not valid is of no importance

Table. *s_m and s_μ as functions of x*

x	s_m	s_μ
$x < 0.1$	$\sim \frac{3}{5}x^3 - x^4$	$\sim \frac{2}{3}x^3 + \frac{2}{15}x^5$
0.1	0.00156	0.00067
0.2	0.01165	0.00538
0.3	0.03657	0.01834
0.4	0.08063	0.04413
0.5	0.1469	0.08802
0.6	0.2379	0.1564
0.7	0.3566	0.2577
0.8	0.5082	0.4045
0.9	0.7039	0.6203
0.95	0.8279	0.7714
0.98	0.9187	0.8890
1.00	1	1

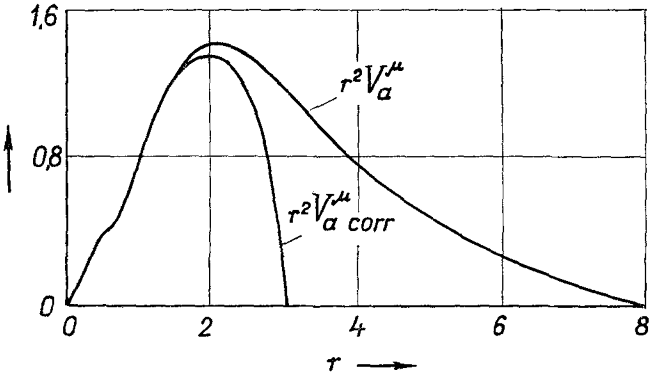

Fig. 1. $r^2 V_a^\mu$ and $r^2 V_{a\,\mathrm{corr}}^\mu$ as functions of r for the K^+ ion. The abscissa and the ordinate in units of a_0 and ea_0 resp.

because in this region both corrections and their approximations are small and can be neglected in comparison with 1.

$V_{a\,\mathrm{corr}}^\mu$ and the uncorrected potential V_a^μ both multiplied by r^2 can be seen in Fig. 1 as functions of the distance r from the nucleus for the case of the Hartree-Fock K^+ ion* (r in units of a_0, $r^2\, V_a^\mu$ and $r^2\, V_{a\,\mathrm{corr}}^\mu$ in units of $e\,a_0$). $V_{a\,\mathrm{corr}}^m$ as a function of r is quite similar to $V_{a\,\mathrm{corr}}^\mu$. For the K^+ ion $V_{a\,\mathrm{corr}}^\mu$ and $V_{a\,\mathrm{corr}}^m$ vanish at $r_g = 3{,}06\, a_0$. By cutting off the exchange potential at $r = r_g$ only $\sim 1{,}5\%$ of one electron is exluded.

The exchange energy between the valence electrons and core electrons in an atom can be calculated with the exchange potential $V_{a\,\mathrm{corr}}^\mu$. The exchange energy for the valence electron for example in the K atom can be obtained from the following expression

$$\varepsilon_{\mathrm{corr}} = -e \int_0^{r_g} V_{a\,\mathrm{corr}}^\mu f_{4s}^2\, dr\,, \tag{7}$$

where $V_{a\,\mathrm{corr}}^\mu$ is the corrected correlation potential of the K^+ ion and f_{4s} is the normalized radial wave function of the valence electron in the $4s$ state of the K atom.

If we insert in this expression for f_{4s} the radial pseudoeigenfunction without nodes of the $4s$ electron of the K atom, which is obtained by replacing the orthogonality of this function to the lower s states by a repulsive pseudopotential [3], we obtain $-0{,}68$ eV for $\varepsilon_{\mathrm{corr}}$. This value is in good agreement with the difference between the experimental and Hartree energies, $-0{,}61$ eV, which is just the exchange energy in question if one disregards the correlation energy of small absolute value**. If, on the other hand, instead of $V_{a\,\mathrm{corr}}^\mu$ we put into (7) the uncorrected potential V_a^μ then we get $-1{,}52$ eV for the exchange energy of the valence electron. The absolute value of this energy is more than twice the correct one. Thus the correction of the exchange potential $V_{a\,\mathrm{corr}}^\mu$ improves in this case essentially the results. Work on more applications is under way.

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* For ϱ the Hartree-Fock density [5] has been used.

** Calculation of E. Mágori and Zs. Ozoróczy, Acta physica Acad. Sci hung. (In press).

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