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Energy Levels in Modified Quantum Statistical Potentials*

JERRY GOODISMAN

Department of Chemistry, Syracuse University, Syracuse, N. Y. 13210, USA

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We calculate one-electron energy levels in potentials derived from the solution of the atomic Thomas-Fermi-Dirac equation. A local exchange potential is used. Corrections are made to a previous theory, which joins a TFD density to a quantum mechanical electron density near the nucleus, where the Thomas-Fermi-Dirac density has an incorrect singularity. Use of a potential derived from this theory leads to improvement in inner-shell energies. Changes in the potential, suggested in the literature as being reasonable for valence electrons, do not always give the expected improvement. Nor does naively correcting for self-energy lead to improved one-electron energy levels in general.

Es werden Einelektronen-Energieniveaus bezüglich Potentialen, die sich aus der Thomas-Fermi-Dirac Gleichung ergeben, berechnet, wobei ein lokales Austauschpotential benutzt wird. Es ergeben sich Korrekturen gegenüber einem früheren Verfahren, bei dem einerseits mit einer TFD Dichte und andererseits der quantenmechanischen Dichte in der Umgebung des Kernes, wo das TFD-Modell ein falsches Verhalten liefert, operiert wird. Auf diesem modifizierten Wege erhält man ein Potential, das zu besseren Funktionen für die inneren Schalen führt. Dagegen ergeben üblicherweise benützte Potentialänderungen für die Valenzelektronen, ebenso wenig wie naheliegende Korrekturen für die Selbstwechselwirkung, nicht die erstrebten Verbesserungen.

1. Introduction

Recently, we have been interested in calculating one-electron energies and wavefunctions in potentials derived from the solution of the Thomas-Fermi-Dirac equations for molecules. Hopefully, this could give results comparable to those of Hartree-Fock calculations but without the necessity of evaluating two-electron integrals or iterating to self-consistency. The potential used was the electrostatic potential which is the solution to the TFD equation (see Eqs. (6) et seq. below) plus an exchange potential proportional to the 1/3 power of the TFD electron density. The potential was modified far from the nuclei to give the proper behavior for an electron moving in the field of the nuclei and all the electrons but one.

The results [1] were qualitatively correct, but definitely inferior in accuracy to the Hartree-Fock. In particular, inner shell orbital energies were too high (by 2 a.u. for the Ar 1s electrons, for instance). We thus want to investigate improvements in the potential, testing these on atoms for simplicity, but requiring that the improvements be applicable to the molecular problem without increasing the complexity of the calculation. (This rules out use of the Weizsacker correction [2], for instance.)

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It is well known that the Thomas-Fermi (TF) and Thomas-Fermi-Dirac (TFD) theories [3], while giving a roughly correct idea of the electron density for atoms, suffer from several serious deficiencies. One of these is that, because of the breakdown of the assumptions of the theory near a Coulombic singularity, they lead to an electron density which goes infinite as $r^{-3/2}$ instead of approaching a constant value as does the correct quantum mechanical density. This suggested to Ashby and Holtzman [4] and to the present author [5] the idea of using a density with the proper behavior for small r, and joining it to a density obtained from solution of the TF or TFD equation for larger r. The modified electron density led ot improved values for several electronic properties in the atomic [5] and molecular [6] cases. It was thought that the modification mentioned could improve the potential as it did the electron density. Examination of the modified theory [5] from the point of view of the potential revealed an inconsistency. In the next section, we give a slightly changed theory which is free from this problem. In Section 3 we calculate eigenvalues in the resulting modified potential.

Recently, Schwarz [7, 8] has pointed out that the Coulomb and exchange energies of the TFD theory actually both include the electrostatic interaction of each electron with itself, and that this self-interaction is a large quantity for atoms (larger [8] than the true exchange energy) where the electrons are localized. While the self-energy terms cancel out in the expression for the total energy, a modification in the potential seen by a single electron, with which we are concerned, is clearly called for. We investigate some simple corrections of this kind in Section 4.

The orbital energies for the valence shell electrons tended to be too low in our preceding work. In this connection, one can argue [9] that the exchange potential employed should be reduced by a factor of 2/3 for these electrons. The exchange potential used by us, given in terms of the density ϱ as $V_a = (3/2)(3/\pi)^{1/3} e\varrho^{1/3}$, may be derived as the *mean* exchange potential for the free-electron gas. However, for electrons with the maximum momentum, *i.e.*, in the highest filled energy state, the same theory gives the exchange potential as $(3/\pi)^{1/3} e\varrho^{1/3}$. This potential has been used successfully [9] to describe atomic valence electrons, and for all the electrons [8] in Hartree-Fock-Slater calculations (where the exchange interaction is approximated by a local exchange potential). The effect of modifying V_a in this way is investigated in Sect. 5.

2. Modified Thomas-Fermi-Dirac Theory

For an atom, let the electron density $\varrho(r)$ be given from $r = 0$ to $r = r_c$, and let the electron density for $r > r_c$ be varied to minimize the energy. Since we will use quantum statistical theories for the energy expression, we may anticipate that the outer boundary of the atom may be at a finite distance. We denote it by r_0, and minimize the energy with respect to r_0 as well as the density for $r > r_c$. The value of r_c is also to be determined.

The following conditions are imposed: (1) Continuity of ϱ at $r = r_c$; (2) continuity of $\mathrm{d}\varrho/\mathrm{d}r$ at $r = r_c$; (3) normalization of the total electron density; (4) vanishing of the electrostatic potential at $r = r_0$; (5) vanishing of the electric field at $r = r_0$. According to the quantum statistical theories [3] the kinetic energy is given by $\int \varkappa_k \varrho^{5/3} \mathrm{d}\tau$ and the exchange energy by $-\int \varkappa_a \varrho^{4/3} \mathrm{d}\tau$. Then the part of the energy which depends on the electron density for $r > r_c$ is

$$E = -Ze^2 \int_{r_c}^{r_0} \varrho r^{-1} \mathrm{d}\tau + \mathscr{J} e^2 \int_{r_c}^{r_0} \varrho r^{-1} \mathrm{d}\tau - \varkappa_a \int_{r_c}^{r_0} \varrho^{4/3} \mathrm{d}\tau$$
$$+ \varkappa_k \int_{r_c}^{r_0} \varrho^{5/3} \mathrm{d}\tau + 1/2 e^2 \int_{r_c}^{r_0} \varrho(r) \,\mathrm{d}\tau \int_{r_c}^{r_0} \varrho(r') \,\mathrm{d}\tau' \, |\boldsymbol{r} - \boldsymbol{r}'|^{-1} . \tag{1}$$

Here, Z is the nuclear charge, $\mathscr{J}$ is the total electron density contained in the sphere $r < r_c$, and the values of the constants in (1) are

$$\varkappa_a = 3/4 (3/\pi)^{1/3} \, e^2 \tag{2}$$

and

$$\varkappa_k = 3/10 (3\pi^2)^{2/3} \, e^2 a_0 , \tag{3}$$

where a_0 is the Bohr radius. The normalization condition for the total electron density is

$$(Z - \mathscr{J}) \, e = e \int_{r_c}^{r_0} \varrho \, \mathrm{d}\tau . \tag{4}$$

We minimize the energy of Eq. (1) keeping the quantity (4) constant by means of a Lagrange multiplier λ. The result is

$$-e^2 (Z - \mathscr{J}) \, r^{-1} - 4/3 \varkappa_a \varrho^{1/3} + 5/3 \varkappa_k \varrho^{2/3} + e^2 \int \mathrm{d}\tau' \varrho(r') \, |\boldsymbol{r} - \boldsymbol{r}'|^{-1} + \lambda e = 0 . \tag{5}$$

Since the electrostatic potential is

$$V = (Z - \mathscr{J}) \, r^{-1} - e \int \mathrm{d}\tau' \varrho(r') \, |\boldsymbol{r} - \boldsymbol{r}'|^{-1} \tag{6}$$

we can rewrite the equation as

$$5/3 \varkappa_k \varrho^{2/3} - 4/3 \varkappa_a \varrho^{1/3} + \mathrm{e}(\lambda - V) = 0 .$$

Combining this with the Poisson equation gives a second order non-linear differential equation for V or ϱ. We go over to the usual dimensionless variables

$$x = r/\mu \tag{7}$$

and

$$\psi = \frac{r}{Ze} (V - \lambda + \tau_0^2) , \tag{8}$$

where

$$\mu = 1/4 (3\pi)^{2/3} \, (2Z)^{-1/3} \, a_0 \tag{9}$$

and

$$\tau_0^2 = 4 \varkappa_a^2 / 15 \varkappa_k e . \tag{10}$$

The differential equation for $r > r_c$ is the usual TFD equation

$$\psi'' = x [(\psi/x)^{1/2} + \beta_0]^3 , \tag{11}$$

where

$$\beta_0 = \tau_0 (\mu/Ze)^{1/2} \tag{12}$$

and the density is given by

$$\varrho = \frac{Z}{4\pi\mu^3} \, [(\psi/x)^{1/2} + \beta_0]^3 . \tag{13}$$

Here, primes mean differentiation with respect to x. The normalization condition is then

$$Z-\mathscr{I}=Z\int_{x_c}^{x_0}(\psi''/x)\,x^2\,\mathrm{d}x=Z(x_0\psi_0'-\psi_0-x_c\psi_c'+\psi_c)\,, \tag{14}$$

where subscripts 0 and c mean values at x_0 and x_c.

We now have to determine r_0 by minimizing the energy expression (1) with respect to this quantity. Because of the conditions (1) and (2) on the density, the differential equation determines ϱ for all $r>r_c$, independently of r_0. Then we need consider only the explicit occurrences of r_0 in Eq. (1). Thus

$$\begin{aligned}\mathrm{d}E/\mathrm{d}r_0=0=&\frac{(-Z+\mathscr{I})\,e^2\varrho_0}{r_0}-\varkappa_a\varrho_0^{4/3}+\varkappa_k\varrho_0^{5/3}\\&+e^2\varrho_0\int_{r_c}^{r_0}\varrho(r')\,\mathrm{d}\tau'|\boldsymbol{r}_0-\boldsymbol{r}'|^{-1}\,.\end{aligned}$$

Here ϱ_0 is the value of the density at $r=r_0$. The last integral is just $(Z-\mathscr{I})/r_0$, so

$$\varrho_0=(\varkappa_a/\varkappa_k)^3 \tag{15}$$

which is eight times the value for the unmodified TFD theory.

Now we impose the conditions that V and $\mathrm{d}\,V/\mathrm{d}r$ must vanish at the boundary of the atom, $r=r_0$. Integrating the Poisson equation inward to some $r>r_c$, we have

$$\begin{aligned}V=&\frac{e}{r}\int_r^{r_0}4\pi r^2\varrho\,\mathrm{d}r-e\int_r^{r_0}4\pi r\varrho\,\mathrm{d}r=er^{-1}\int_x^{x_0}Zx\psi''\,\mathrm{d}x\\&-e\mu^{-1}\int_x^{x_0}Z\psi''\,\mathrm{d}x=(eZ/r)\,(x_0\psi_0'-\psi_0+\psi-x\psi_0')\,.\end{aligned}$$

Now this must equal $Ze\psi/r+\lambda-\tau_0^2$ according to (8), so we have

$$\lambda-\tau_0^2=\frac{Ze}{r}\,[x_0\psi_0'-\psi_0-x\psi_0']\,.$$

Since λ, τ_0^2, x_0, ψ_0', and ψ_0 are constants, this can hold for all r between r_c and r_0 only if

$$x_0\psi_0'-\psi_0=0 \tag{16}$$

and

$$\lambda-\tau_0^2=-Ze\psi_0'/\mu\,. \tag{17}$$

The condition (16) is automatically satisfied for the unmodified TFD theory, as is seen by putting $x_c=0$, $\mathscr{I}=0$, and $\psi_c=1$ in (14). In the present case, ψ_c and ψ_c' will be chosen to assure continuity of ϱ and $\mathrm{d}\varrho/\mathrm{d}r$ at r_c, assuming a particular density ϱ for $r<r_c$. We must satisfy (14), (16), and (17). The available parameters are r_c and λ. Combining (14) and (16) allows one to calculate r_c, and the cut-off point is determined by normalization, so can no longer be chosen by the variational criterion. λ is fixed by (17).

In the original modified theory [5], the small-r density was assumed to be that of the inner shell electrons. Thus

$$\varrho(r<r_c)=\frac{2Z^3}{\pi}\,e^{-2Zr} \tag{18}$$

which corresponds to two 1*s* electrons moving in the field of the nucleus. Then

$$\mathscr{I} = 2[1 - e^{-2Zr_c}(1 + 2Zr_c + 2Z^2 r_c^2)]\,.$$

According to (14) and (16),

$$1 - Z^{-1}\mathscr{I} = -x_c \psi_c' + \psi_c \tag{19}$$

and from (13)

$$\psi_c = \left[\left(\frac{4\pi\mu^3 \varrho_c}{Z}\right)^{1/3} - \beta_0\right]^2 x_c\,. \tag{20}$$

Insertion of (18) into (20) and differentiation allows computation of the right side of (19) as a function of r_c. Then (19) may be solved numerically for r_c. When this procedure is performed for Ar, it is found that r_c must be 0.0422 a_0 and that $\psi_c = 0.7904$ and $\psi_c' = -0.1573$. If this is integrated outward, the electron density remains large out to r_0 so that it has a large discontinuity at this point, which is physically unacceptable.

To get something more reasonable for this model and to satisfy the condition of Eq. (15) for ϱ_0, it is necessary to relax one of the conditions we have imposed. For the density of (18) we substitute αe^{-2Zr} with the coefficient α to be determined. Unlike Ashby and Holtzman [4], who used the density $\varrho = \alpha e^{-\beta r}$ for $r < r_c$ with both α and β variable, we maintain $\beta = 2Z$ to give the known correct behavior of the density at the nucleus (cusp condition) [10].

Now our procedure is as follows: (i) For a given α we find x_c by demanding that (19) be fulfilled. This is done by computing ϱ and ϱ' for different values of x, and from them deriving $\mathscr{I}$, ψ_c, and ψ_c'. (ii) Now one has initial values for ψ and ψ' and can integrate (11) outward. The integration is stopped at x_0 such that (16) is obeyed. (iii) ψ_0 and ψ_0' are now known, and ϱ_0 may be computed from (13). If (15) is not obeyed, α is changed and the process is repeated until it is. (iv) From ψ_0', λ may be computed according to (17). Now one knows V between r_c and r_0 according to (8). (v) For $r < r_c$, V is obtained by integrating the Poisson equation inward, using $\varrho = \alpha e^{-2Zr}$. Explicitly, this gives

$$V = \frac{\pi\alpha}{Z^3 r}[-1 + e^{-2Zr}(1 + Zr)] + \frac{Z}{r} + \frac{\pi\alpha}{Z^2} e^{-2Zr}(1 + 2Zr_c) - \frac{Z}{\mu}(\psi_0' - \psi_c')\,. \tag{21}$$

3. Orbital Energies in Modified Potential

Having determined the electrostatic potential V according to the above procedure, we add the exchange potential

$$V_a = 3/2\,(3/\pi)^{1/3}\, e\varrho^{1/3} \tag{22}$$

to form the potential to be used in the calculation of one-electron energies. The density ϱ is $\alpha \cdot e^{-2Zr}$ for $r < r_c$ and the TFD density (13) for $r > r_c$. As we have mentioned, Eq. (22) represents an average exchange potential for all the electrons. The total exchange energy density (Eqs. (1) and (2)) is $-1/2\,\mathrm{e}V_a \varrho$, the factor of 1/2 correcting the fact that the interaction between each pair of electrons is otherwise counted twice. For a neutral system, the total potential seen by one electron must become Coulombic at large distances from the nuclei. This is assured for the present

Table 1. Orbital energies for F in a.u. (Per cent differences from experimental results in parentheses)

	Experimental (Ref. [11])	SCF[1]	Unmodified TFD (Ref. [1])	Modified TFD (Section 3)
$1s$	−25.6	−26.38 (3.0)	−25.38 (0.9)	−26.01 (1.6)
$2s$	− 1.48	− 1.57 (6.0)	− 1.68 (13.5)	− 1.63 (10.1)
$2p$	− 0.96	− 0.73 (6.0)	− 0.96 (39.0)	− 0.93 (35.0)

Table 2. Orbital energies for Ar in a.u. (Per cent difference from experimental results in parentheses)

	Experimental (Ref. [11])	SCF (Ref. [12])	Unmodified TFD (Ref. [1])	Modified TFD (Section 3)
$1s$	−118.1	−118.6 (0.4)	−116.4 (1.4)	−117.9 (0.2)
$2s$	− 12.1	− 12.32 (1.8)	− 11.54 (4.6)	− 11.66 (3.6)
$2p$	− 9.25	− 9.58 (3.6)	− 9.31 (0.6)	− 9.41 (1.7)
$3s$	− 1.08	− 1.28 (18.5)	− 1.08 (0.0)	− 1.01 (6.5)
$3p$	− 0.58	− 0.59 (2.0)	− 0.62 (.0)	− 0.53 (10.0)

case by replacing $V+V_a$ by er^{-1} whenever it falls below er^{-1}. This was done by Latter[1] in his computations for a related problem.

In Table 1 we give orbital energies for F, as derived from the present theory, the unmodified TFD theory [1], SCF calculations [11] and experiment [12]. The values found for α and r_c were 356.845 and $0.1015763a_0$. An improvement for the inner shell electrons due to the modification is evident and expected: the error goes from 3.8 % to 1.4 % relative to the SCF result. For the other electrons, the modification also gives improvement, but it is slight for the $2p$ electrons, where the error is most serious. We believe that the fact that the SCF is farther from experiment than either TFD result for $1s$ is a coincidence for this case. Table 2 gives similar results for Ar. Here, $\alpha = 3134.98$ and $r_c = 0.0476648a_0$. The K-shell energy here is in error by 0.2 % relative to SCF, compared to 1.4 % for the unmodified TFD theory. Other energies are sometimes improved, sometimes not; those for the outer electrons (M-shell) are relatively little affected. It may be noted that, in general, while inner shell orbital energies are lowered by the modification, outer shell energies are raised. In addition, the SCF does not reproduce the experimental term values as well as either TFD theory. The average per cent errors for the five levels are 5.2 for SCF, 2.7 for TFD and 4.5 for the modified TFD.

For the orbitals themselves we give in Table 3 the values of r for which nodes and extrema occur in the case of Ar. These are compared with the results of a Hartree-Fock calculation. The functions involved are actually r times the true radial wavefunctions. Since our method of determining the energies [1] involves outward numerical integration of the one-electron Schrödinger equation, our wavefunctions are less precisely determined at larger r. In particular, their tails are inaccurately determined, making it difficult to compute expectation values for the orbitals. It is seen that they have roughly the correct shapes.

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[1] Latter, R.: Physic. Rev. **99**, 510 (1955). The potential used by Latter was an approximation to $V+V_a$; the difference between the approximation and the potential leads to important differences in the computed energy levels as shown in Ref. [1].

Table 3. Characteristics of orbitals for Ar, distances in a_0[a]

Orbital	Extremum	Node	Extremum	Node	Extremum
1s	0.057	—	—	—	—
	0.051				
2s	0.045	0.118	0.34		
	0.039	0.102	0.28		
2p	0.29				
	0.24				
3s	0.044	0.115	0.29	0.52	1.19
	0.039	0.101	0.25	0.44	1.0
3p	0.22	0.42	1.29		
	0.19	0.40	1.10		

[a] First line is SCF from Czyzak, S.J.: Astrophys. J. Supp. 65, 7, 53 (1962); second is our result.

Table 4. Orbital energies for Zn, a.u. (Per cent deviation from experiment in parentheses)

Orbital	Experiment (Ref. [11])	This calculation	Herman and Skillman, Ref. [13]
1s	-356.0	-352.5 (0.8)	-349.2 (1.9)
2s	-44.4	-44.2 (0.5)	-42.56 (4.1)
2p	-38.1	-39.6 (3.9)	-37.78 (0.8)
3s	-5.2	-6.22 (20.)	-4.89 (6.)
3p	-3.5	-4.64 (33.)	-3.33 (5.)
3d	-0.64	-1.82 (180.)	-0.63 (1.6)
4s	-0.34_5	-0.51 (48.)	-0.309 (10.)

It is of interest to compare our results with those of the Hartree-Fock-Slater calculations of Herman and Skillman [13], a self-consistent field procedure in which a local approximation to the exchange potential is used. Their orbital energies are slightly better than ours for the outer shells, but inferior for the rest. The results for the orbitals are similar. The positions of the first extremum for the five orbitals are 0.057, 0.044, 0.28, 0.044, 0.22. This agrees very well – better than our results – with the SCF. The positions of the second extremum for 2s, 3s, and 3p are also in good agreement with SCF.

Finally, we give results for the 30-electron atom: Zn. Table 4 gives our calculated orbital energies, experimental ionization potentials, and the orbital energies of Herman and Skillman. Again, we do well for the inner shells and poorly for the outer electrons. Indeed, the errors for these orbital energies are very large, all being much too low. The evidence is, however, that *the small-r modification is successful in correcting the incorrect behavior of the potential as it affects the inner shell electrons, and permits reliable values to be calculated for inner-shell ionization potentials.*

4. Self-Energy Corrections

In this section, we investigate the effect on the one-electron energy levels of simple modifications of the Coulomb and exchange potentials, designed to remove incorrectly included self-energy terms. These would cancel for a correct Hartree-

Table 5. Energy levels for Ar (atomic units) with V_a, $(1-2Z^{-1})^{1/3}\ V_a$ and $(1-2Z^{-1})\ V_a$[a] compared with SCF values[b]

Atomic orbital	With full V_c and V_a	With $V_c x$ $(1-Z^{-1})$ and $V_a(1-2Z^{-1})^{1/3}$	With $V_c x$ $(1-Z^{-1})$ and $V_a(1-2Z^{-1})$	SCF result
1*s*	−116.4	−118.1	−117.4	−118.60
2*s*	− 11.54	− 12.97	− 12.70	− 12.32
2*p*	− 9.31	− 10.78	− 10.52	− 9.58
3*s*	− 1.08	− 1.76	− 1.64	− 1.28
3*p*	− 0.62	− 1.19	− 1.13	− 0.59

[a] The Coulombic potential is multiplied by $1-Z^{-1}$ in the latter two cases.

[b] Czyzak, S. J.: Astrophys. J. Supp. 65, 7, 53 (1962).

Fock potential. For the Coulombic potential V_c, a simple and reasonable approximation is to multiply the electronic contribution to the electrostatic potential by $(Z-1)/Z$, Z being the number of electrons [7].

The correction to be made on the exchange potential is perhaps more problematical. Schwarz [8], following a suggestion of Gombás [14], favors reducing ϱ by $(Z-2)/Z$, noting that only half the electrons have an exchange interaction with any given electron. This menas V_a is to be multiplied by $(1-2Z^{-1})^{1/3}$. We think it is equally reasonable to argue that the potential itself should be multiplied by $(1-2Z^{-1})$. We may also note that Schwarz's V_a is only 2/3 of ours. Whether the factor of 3/2 does or does not appear in V_a may depend [7] on at what stage in the derivation one introduces the free-electron-gas model (but see next section). Irrespective of the coefficient of $\varrho^{1/3}$ in the exchange potential, the factor of $(1-Z^{-1})$ multiplying V_c assures that the overall potential approaches r^{-1} for large r as it should, with no additional modification.

In Table 5 we give the energies of the occupied one-electron levels for Ar, calculated with the unmodified TFD, with SCF, and the energies calculated when the Coulombic potential is multiplied by $1-Z^{-1}$ with the exchange potential reduced either by $(1-2Z^{-1})$ or by $(1-2Z^{-1})^{1/3}$. All energies are in atomic units (one a.u. = 27.21 eV).

It may be seen that the energies with the full V_c and V_a (and V replaced by r^{-1} when it falls below r^{-1}) are in fair agreement with the SCF values (average error = 6%). Modification of V_c and V_a in either way lowers all the energy levels and makes the overall agreement worse, although improving the 1*s* and 2*s* energies. We feel that the problem here is that the unmodified TFD model puts too much electron density near the nucleus. (The modification of Sections 2 and 3 lowers this density markedly.) Then the effective nuclear charge is too low near the nucleus, so that orbital energies will be too high for orbitals whose density is large here. Reducing V_c raises the effective charge everywhere, improving inner shell orbitals but overcompensating errors in others.

The situation may be contrasted with calculations such as those of Schwarz [8] or Herman and Skillman [13], where the exchange potential or some modification of it is used in SCF calculations to avoid the complications of the non-local Hamiltonian. There, the Coulombic potential includes correct behavior of the electron density near the nucleus. No iteration to self-consistency is involved in our work. Still, it is interesting to note that the errors in the orbital energies, using the full V_c and V_a, are comparable to those made in the approximate calculations. Schwarz [8] has given an extensive summary of such results for Ar. Our per cent errors are 1.9, 6.3, 2.8, 15.6, and 5.1; only about half of the ten methods tried by Schwarz do as well overall.

A recent article by Slater and Wood [15] discusses SCF calculations using local exchange approximations. The reason that good atomic orbitals, but poor orbital energies, are obtained in some cases (see end of Section 3) is explained. The orbital energy in Hartree-Fock calculations represents the change in energy on removal of one electron (Koopmans' Theorem), whereas in the calculations using local exchange potentials the orbital energy is the derivative of total energy with respect to the number of electrons. The difference may be written as a power series in which the derivative is the leading term, and higher terms may be used to give corrections. In the present case, where the potential is not constructed from the orbitals, the errors in orbital energies merely reflect the errors in the potential itself.

5. Modifications for the Valence Electrons

For some purposes, the valence electrons or electrons in the highest filled shell are of greatest interest. Thus we are interested in methods which may give reliable values for these. The errors in the present results are serious. We wish to explore methods for obtaining better values for the valence electrons, keeping in mind that our object is to apply such methods, eventually, to molecules with many electrons.

Errors in our potential for large r are of importance here. In particular, the effect of simply putting on a Coulombic tail must be examined. Yonei [16] remarked that the resulting discontinuity in $\mathrm{d}V/\mathrm{d}r$ may be of importance. Since we are interested in an electron moving in the field of the nucleus plus the other electrons, we could calculate their distribution and potential, and use this potential to treat the electron of interest. This automatically gives the correct large-r behavior with no discontinuity in $\mathrm{d}V/\mathrm{d}r$.

For the atom of atomic number Z, one should solve the TFD problem for the positive ion of nuclear charge Z and with $Z-1$ electrons. Then the electrostatic potential from this solution should be used, together with V_a derived from the electron density of the ion, to compute one-electron eigenvalues. Since the boundary conditions for the TFD equation change with degree of ionization [4] we have not done this. If one assumes the density for K^+ is well-approximated by that of Ar, one can use the Ar potential plus er^{-1} to obtain one-electron energies for K. The results were not good: orbital energies were always too low. This ignores the contraction of ϱ due to the additional nuclear charge, which increases the electrostatic shielding.

As we have mentioned, the exchange potential may be derived by averaging the exchange energy expression for an electron in a free-electron gas over all the electrons. One can also consider electrons with specific momenta individually, without averaging. For an electron with $p=0$, one obtains $2(3/\pi)^{1/3}e\varrho^{1/3}$ for the potential representing its exchange interaction with all the others. For an electron with p equal to the Fermi momentum, one gets half this. The last result is relevant for consideration of valence electrons, which are the highest filled orbitals. It may also be derived from the expression for the exchange energy density, $\varkappa_a \varrho^{4/3}$, by considering the effect of adding a small number of electrons, which must be at the Fermi momentum. The change in exchange energy density with change in ϱ is

$$\mathrm{d}(-\varkappa_a e^2 \varrho^{4/3})/\mathrm{d}(-e\varrho) = 4/3\, \varkappa_a e \varrho^{1/3}$$

so that $V_a = 4/3\, \varkappa_a e \varrho^{1/3}$ for these electrons.

Maintaining the small r modification of Sections 2 and 3, we change our exchange potential as above. For F, the $2p$ energy level goes from -0.93 a.u. to -0.52 a.u., which is equally far from the SCF value of -0.73 a.u. Now the $2p$ electrons represent 5/9 of the total number, so that the argument for using a potential appropriate to the top of the Fermi sea is not well-justified here. For Ar, the $3p$ electrons are 6/18 of the total, so the situation is somewhat better from the point of view of justification. Unfortunately, ε_{3p} is already too high and the modification must make things worse. In fact it goes to about -0.3 a.u.

However, for Zn, this modification leads to $\varepsilon = -0.32_2$ for the $4s$ orbital energy which is closer to the experimental orbital energy than the result of Herman and Skillman. The $3d$ energy increased to above -1. It is for this atom that one expects this idea to work best, since (a) the number of electrons is greatest and (b) the valence electrons are the smallest fraction (1/15) of the total number. The result is encouraging: in the future, we hope to extend these calculations to larger atoms and then to molecules, to see whether the results for Zn are typical.

References

1. Goodisman, J.: Theoret. chim. Acta (Berl.). Submitted for publication.
2. Yonei, K., Tomishima, Y.: J. Physic. Soc. Japan **20**, 1051 (1965).
3. Gombás, P.: Die statistische Theorie des Atoms und ihre Anwendungen, Vienna: Springer 1949.
4. Ashby, N., Holtzman, M. A.: Physic. Rev. A **1**, 764 (1970).
5. Goodisman, J.: Physic. Rev. A **2**, 1193 (1970).
6. — Physic. Rev. A **3**, 1819 (1971).
7. Schwarz, W. H. E.: Z. Physik **214**, 149 (1968).
8. — Z. Physik **239**, 162 (1970).
9. Gombás, P.: Pseudopotentiale, Wien-New York: Springer 1967.
10. Steiner, E.: J. chem. Physics **39**, 2365 (1963).
11. Clementi, E.: IBM J. Res. Devel. **9**, 2 (1965), supplement.
12. Slater, J. C.: Physic. Rev. **98**, 1039 (1955).
13. Herman, F., Skillman, S.: Atomic structure calculations, Englewood Cliffs, New Jersey: Prentice-Hall 1963.
14. Gombás, P.: Theoret. chim. Acta (Berl.) **5**, 112 (1966).
15. Slater, J. C., Wood, J. H.: Int. J. quant. Chemistry **4**, 3 (1971).
16. Yonei, K.: J. Physic. Soc. Japan **22**, 1127 (1967).

Prof. Dr. J. Goodisman
Department of Chemistry
Syracuse University
Syracuse, N.Y. 13210, USA