ON CENTRAL FIELD MODELS OF THE ATOM

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A simple redefinition of the potential energy assigned to a particular electron in the central field model of the atom removes the couplings of the single particle Schrödinger equations describing electrons in atoms. It leads to the validity of the same virial theorem for a particular electron as it is valid for the whole atom. The model makes a useful separation of the single particle potential energy operator into local and nonlocal parts. The method is based on the fact that the parameters appearing in the potential energy operators are rather insensitive to the detailed radial shape of wave functions.

1. Introduction

Central field models have been extensively employed for the description of atomic structure. But simple models, such as various hydrogenic models, or the Thomas-Fermi model, have been far less successful than the Hartree (-Fock) model[1]. Recently a new version of the hydrogenic model, the independent particle model (*IPM*) based on an unconventional sharing of the potential energy of interacting particles, has been proposed[2,3]. It is our aim to compare this model with other central field models and with the Hartree model specifically. This comparison leads to an interesting interpretation of the independent particle potential energy, as well as to the validity of the same virial theorem for a particular electron, as is valid for the whole atom.

Though in the *IPM* presented in Refs. 2 and 3, the exchange interaction is also taken into account, we shall neglect it in the presentation of the basic idea. It is however assumed that the occupancy of electronic states obeys the Pauli principle. But before making quantitative comparison with experimental or Hartree--Fock results, the exchange interaction effect will be included in the same sense as was done in Refs. 2 or 3.

2. *The IPM versus the Hartree central field model*

In central field models (*CFM*) of the atom we usually approximate the two body potential energy operator of the atomic Hamiltonian

$$H = \sum_s \left(\frac{p_s^2}{2m} - \frac{Z}{r_s} \right) + \sum_{t>s} \sum \frac{1}{r_{s,t}} \tag{1}$$

by single particle potential energy terms of the form $\sum_s \bar{U}(r_s)$. Most often the potential

$$\overline{W}_s(r_s) = - \frac{Z}{r_s} + \bar{U}(r_s) = - \frac{Z}{r_s} \chi(r_s) \tag{2}$$

is referred to as the screened single particle Coulomb potential. It is further assumed that the condition

$$\lim_{r_s \to 0} \chi(r_s) = 1 \tag{3}$$

must be satisfied.

According to Hartree the single particle potential energy operators are

$$\bar{U}(r_s) = \sum_{t \neq s} \int \frac{1}{r_{s,t}} |\Psi(r_t)|^2 \, dV_t \tag{4}$$

where $|\Psi(r_t)|^2$ represents the spherically averaged electron density of the t-th electron ($t \neq s$). In such a procedure the electron-electron interaction of the atom is counted twice and the corresponding set of single particle Schrödinger equations

$$\overline{H}_s|s\rangle = \left(\frac{p_s^2}{2m} - \frac{Z}{r_s} + \bar{U}(r_s) \right) |s\rangle = E_s|s\rangle \tag{5}$$

is coupled. According to Hartree, Eqs. (5) are variational equations, which minimize the expression $\langle \Psi | \sum_s H_s | \Psi \rangle / \langle \Psi | \Psi \rangle = 0$, where $|\Psi\rangle = \prod_s |s\rangle$ is the non-symmetrized atomic wave function.

The need for the variational procedure required by the Hartree method, is avoided by the independent particle model (*IPM*) approach. Below we present an approach to the *IPM* which is less heuristic than those given in Refs. 2 or 3.

It is our aim to show that a spherical average of the sum of the two body operators $\sum_t \sum_s 1/r_{s,t}$ in (1) is not conveniently represented by the sum $\sum_s \overline{U}(r_s)$, but should be rather sought in the form

$$\sum_s U_s(r_s, r_t) = \sum_s [U_s(r_s) + \sum_{t \neq s} V_s(r_t)]. \tag{6}$$

The thus defined single particle potential energy operator, replacing (4), is obviously split into the *local* and *nonlocal* parts

$$U_s(r_s, r_t) = U_s(r_s) + \sum_{t \neq s} V_s(r_t). \tag{7}$$

Its physical meaning will be more thoroughly investigated below.

Such a redefinition leads to single particle Schrödinger equations of the form

$$\left(\frac{p_s^2}{2m} - \frac{Z}{r_s} + U_s(r_s) + \sum_t V_s(r_t)\right)|s\rangle = E_s|s\rangle. \tag{8}$$

But the terms $V_s(r_t)$ do not affect the state $|s\rangle$, since they are independent of r_s. So they can be conveniently moved to the right hand side of Eq. (8) if we integrate (8) over coordinates of all electrons other than the s-th electron. So we arrive at

$$H_s|s\rangle = \left(\frac{p_s^2}{2m} - \frac{Z}{r_s} + U_s(r_s)\right)|s\rangle = [E_s - \sum_{t \neq s} \langle t|V_s(r_t)|t\rangle]|s\rangle = W_s^0|s\rangle. \tag{9}$$

The proposition (7) is meaningful if $U_s(r_s, r_t)$ can be conveniently split into local and nonlocal parts such that a set of Equations (9) will represent a set of decoupled, independent particle Schrödinger equations. Below we shall show that such a splitting can easily be done, provided some physically justified approximations are made.

To simplify the discussion, we shall consider for a while a simplified atom, consisting of only two occupied shells (the generalization to more shells is straight-forward). Let the lower shell accomodates P electrons denoted by i, or i', while the upper shell accomodates M electrons denoted by j or j' (they all obey Pauli principle), as is schematically represented in Fig. 1. According to the central field approximation, the potential experienced by individual electrons is spherically symmetrical.

Then we may introduce the internal screening parameter f_t and the external screening parameter g_s in the following way

$$\langle s, t| 1/r_{s,t}| s, t\rangle = g_s \langle s |1/r_s| s\rangle + f_t \langle t |1/r_t| t\rangle \tag{10}$$

where both electrons belong either to the same shell, or t-electron is the external one with respect to the s-electron. (This definition of f_t differs somewhat from that in Refs. 2 and 3, where g_s was taken to be zero.)
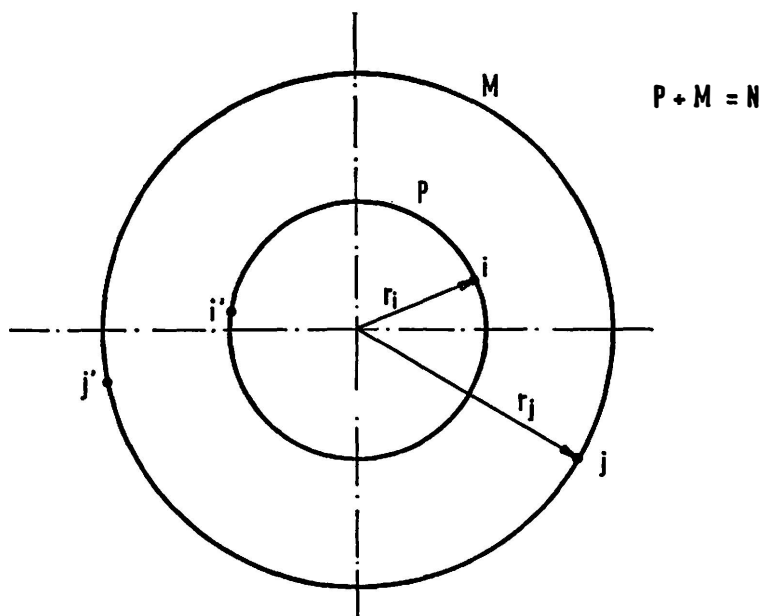
1. Schematic representation of the atom with two shells and with P and M electrons in respective shells.
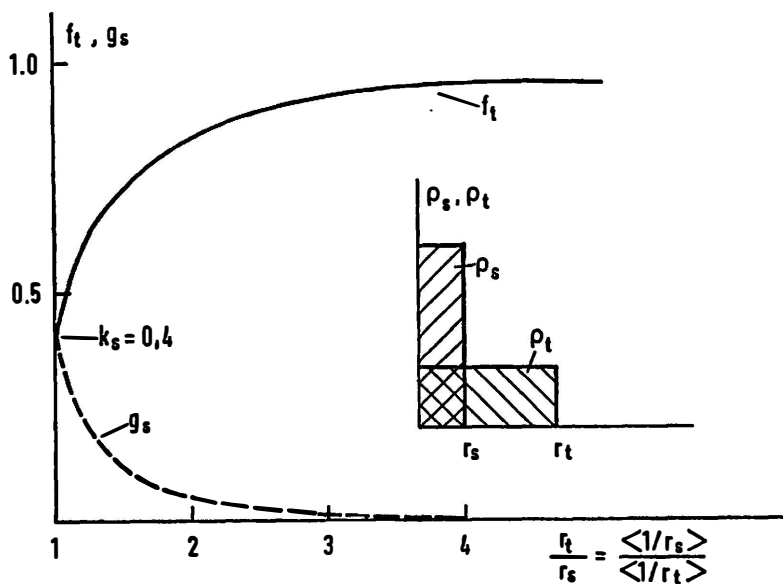
2. The $\langle 1/r_s \rangle / \langle 1/r_t \rangle$ dependence of the screening parameters f_t and g_s for s- and t-electrons with uniform charge distributions up to maximum radii r_s and r_t, respectively. (See also Appendix.)

For the electron pair with electrons in well separated shells, $g_s = 0$ and $f_t = 1$. On the other hand, for electrons belonging to the same (sub)shell,

$$g_s = f_t = k_s.$$

It was shown in Refs. 2 and 3 that parameters f_t and k_s are rather insensitive on the particular electronic configuration of the atom, as well as of the atomic number Z and can be therefore regarded as constants. This fact is also demonstrated in Fig. 2, where the dependence of f_t and g_s on the ratio of respective radii r_t/r_s is shown for electrons described by constant charge densities within r_s and r_t, respectively (see also Appendix).

The atom, presented in Fig. 1, is therefore described by parameters k_i, k_j, g_i and f_j. They are weakly dependent on P, M or Z, but may depend on n_s and l_s.

We will further assume that these parameters are independent of $\langle r_i \rangle$, or $\langle r_j \rangle$. The validity of this assumption is investigated in the Appendix.

Then the two particle interaction energy matrix elements can be expressed in terms of the simple single particle matrix elements[2, 3]

$$\langle i, i' \,|1/r_{i,i'}|\, i, i' \rangle = \langle i \,|k_i/r_i|\, i \rangle + \langle i' \,|k_i/r_{i'}|\, i' \rangle. \tag{11a}$$

Similarly

$$\langle j, j' \,|1/r_{j,j'}|\, j, j' \rangle = \langle j \,|k_j/r_j|\, j \rangle + \langle j' \,|k_j/r_{j'}|\, j' \rangle. \tag{11b}$$

But

$$\langle j, i \,|1/r_{i,j}|\, j, i \rangle = \langle j \,|f_j/r_j|\, j \rangle + \langle i \,|g_i/r_i|\, i \rangle. \tag{11c}$$

Here i and i' denote electrons in the lower shell and j or j' those in the upper shell. (In the following an average k_s as well as an average f_j value will be used for particular (sub)shell. For more details concerning definitions and the determination of these average values, see Ref. 3).

Having definitions (11a—c) in mind, in the central field approximation we may replace the two particle potential energy operators $1/r_{s,t}$ by the single particle operators

$$1/r_{i,i'} \rightarrow k_i/r_i + k_i/r_{i'},$$

$$1/r_{j,j'} \rightarrow k_j/r_j + k_j/r_{j'},$$

$$1/r_{i,j} \rightarrow f_j/r_j + g_i/r_i.$$

It is essential that e. g. $1/r_{i,i'}$ is not replaced by $2k_i/r_i$ (as would correspond to the Hartree approach), but by an operator symmetric with respect to both electrons. Similarly, $1/r_{i,j}$ is replaced by single particle operators which operate separately on each of the two electrons.

Then the single particle operators $U_s (r_s, r_t)$, representing the spherical average of the sum $\sum\limits_t 1/r_{s\,t}$ are

$$U_i (r_i, r_t) = U_i (r_i) + \sum_{t \neq i} V_i (r_t) \tag{12a}$$

where

$$U_i(r_i) = (k_i(P-1) + g_i M)/r_i$$

$$\sum_{t \neq i} V_i(r_t) = \sum_{i'}^{P-1} k_i/r_{i'} + \sum_j^M f_j/r_j \tag{12b}$$

for the i-th electron in the lower shell. Similarly

$$U_j(r_j, r_t) = U_j(r_j) + \sum_{t \neq j} V_j(r_t) \tag{13a}$$

where

$$U_j(r_j) = (Pf_j + k_j(M-1))/r_j \tag{13b}$$

$$\sum_{t \neq j} V_j(r_t) = \sum_{j'}^{M-1} k_j/r_j + \sum_i^N g_i/r_i$$

Operators (12a—b) therefore replace the single particle operators $\overline{U}(r_s)$ in Eqs. (2), (4) and (5). They are distinctly separated into *local* and *nonlocal* parts, as required by (7). Adding the local part $U_s(r_s)$ to the central nuclear potential $-Z/r_s$, we write (9) explicitly as

$$\left(\frac{p_i^2}{2m} - \frac{Z_i}{r_i}\right)|i\rangle = W_i^0|i\rangle; \quad Z_i = Z - k_i(P-1) - g_i M \tag{14a}$$

and

$$\left(\frac{p_j^2}{2m} - \frac{Z_j}{r_j}\right)|j\rangle = W_j^0|j\rangle; \quad Z_j = Z - f_j P - k_j(M-1) \tag{14b}$$

for the i-th and j-th electron, respectively.

So the Hamiltonian (1) is replaced by $(P + M)$ independent particle Hamiltonians, leading to the independent particle Schrödinger equations (14a—b), describing independently moving quasielectrons, carrying the charge Z_s/Z, in the non-screened Coulomb potential of the atomic nucleus. The solutions of (14a—b) are therefore hydrogen like

$$\Psi_s = \langle r_s|s\rangle = R_{nl}(Z_s r_s) Y_{l,m}(\vartheta_s, \varphi_s) \tag{15}$$

with the independent particle energies

$$W_s^0 = -Z_s^2/2n_s^2. \tag{16}$$

Results (14) to (16) were already given in Ref. 3. But this derivation reveals the splitting of the single particle potential energy operator into its local and nonlocal parts.

According to this *IPM* approach the (local part of the) independent particle potential energy of the particular electron is twice as much as the independent particle energy W_s^0

$$\langle W_{p,s}^0 \rangle = \langle s \,|-Z/r_s + U_s(r_s)|\, s \rangle = \langle s \,|-Z_s/r_s|\, s \rangle = -\, Z_s^2/n_s^2 = 2W_s^0. \tag{17}$$

Because the independent particle kinetic energy is $\langle W_{k,s}^0 \rangle = W_s^0 - \langle W_{p,s}^0 \rangle = = -\langle W_{p,s}^0 \rangle/2$, the independent particle virial theorem

$$2\langle W_{k,s}^0 \rangle + \langle W_{p,s}^0 \rangle = 0 \tag{18}$$

is valid for each electron. Simultaneously, the virial theorem for the whole atom

$$2\langle W_k^0 \rangle + \langle W_p^0 \rangle = 0 \tag{19}$$

with $\langle W_k^0 \rangle = \sum\limits_{s}^{P+M} \langle W_{k,s}^0 \rangle$ and $\langle W_p^0 \rangle = \sum\limits_{s}^{P+M} \langle W_{p,s}^0 \rangle$ is valid as well.

According to this view, the potential energy operator describing the potential energy of the nucleus, is wholly nonlocal. Assigning to the atomic nucleus $s = 0$, we have

$$\sum_{t} V_0(r_t) = -\sum_{t=1}^{P+M} Z/r_t$$

and therefore the local part of the potential energy $\langle W_{p,0}^0 \rangle$ of the nucleus is zero. Therefore (18) is valid for the atomic nucleus as well, and (19) holds with the atomic nucleus included.

Atomic energy is then a simple sum of independent particle energies

$$W^0 = \sum_{s=0}^{P+M} W_s^0.$$

Let us compare the independent particle energies W_s^0 with the single particle energies E_s. The kinetic energy being the same in the *IPM* and Hartree description, the difference $E_s - W_s^0$ may be regarded as the nonlocal part of the single particle potential energy of the s-th electron

$$W_{p,s}^n = \sum_{t \neq s} \langle t \,|\, V_s(r_t) \,|\, t \rangle.$$

This energy is not included in $\langle W_{p,s}^0 \rangle$. According to (9) we find explicitly for the lower shell electrons

$$W_{p,i}^n = E_i - W_i^0 = \sum_{i'}^{P-1} \langle i' \,|k_i/r_{i'}|\, i' \rangle + \sum_{j}^{M} \langle j \,|f_j/r_j|\, j \rangle = k_i(P-1)Z_i/n_i^2 +$$

$$+ f_j\, M\, Z_j/n_j^2. \tag{20a}$$

Similarly we find for the upper shell electrons

$$W_{p,J}^n = E_J - W_J^0 = k_J (M-1) Z_J/n_J^2 + g_l P Z_l/n_l^2 \qquad (20b)$$

In atomic physics many atomic properties are expressed in terms of single particle and two particle energy integrals. They are usually calculated using powerful computers. But in the independent particle model they assume a very simple form. Expressions for some basic energy integrals, as are given by the *IPM*, in standard notation are, as follows:

$$KE(s) = \langle s\,|p_s^2/2m|\,s\rangle = \langle W_{k,s}\rangle = Z_s^2/2n_s^2 \qquad (21a)$$

$$PE(s) = \langle s\,|Z/r_s|\,s\rangle = \langle W_{p,s}\rangle\, Z/Z_s = ZZ_s/n_s^2 \qquad (21b)$$

$$I(s) = \langle s\,|p^2/2m - Z/r_s|\,s\rangle = Z_s(Z_s - 2Z)/2n_s^2 \qquad (21c)$$

$$F^0(s,t) = \langle s\,t\,|1/r_{s,t}|\,s,t\rangle = g_s Z_s/n_s^2 + k_t Z_t/n_t^2. \qquad (21d)$$

The latter integral (21d) is valid only if both electrons belong to the same shell. If they do not, only the energy integrals F^0 for the lowest n_s are simple, as for example

$$F^0(1s, 21) = f_{21} Z_{21}/4. \qquad (21e)$$

The value of the energy integral for the potential energy $PE(s)$ follows from the properties of wave functions (15), that for kinetic energy, $KE(s)$ follows from the virial theorem (18). $I(s)$ is a simple combination of both. Integrals $F^0(s,t)$ with both electrons belonging to the same shell directly define the electron interaction constant k_s. Similarly, the screening constant f_J is defined by (21e), if g_l is zero.

The *IPM* thus avoids the variational procedure. But it requires knowledge of the electron interaction constants k_s, g_s and f_s, which in turn define Z_s.

A simple version of the *IPM* was proposed already in 1930[4]. Recently several examples of the applicability of the *IPM* were given in Refs. 2 and 3. The model presented there also takes into account the exchange interaction effect within each shell separately. This effect was here disregarded for the sake of clarity presentation. But it can easily be included by replacing expression $k_l(P-1)$ in (14a) and (20a) by a more general expression

$$k_l\{(P-1) - \varepsilon_l((3/4)(P-2) + S_l(S_l+1)/P)\} \qquad (22a)$$

where ε_l is the exchange interaction constant for that shell* and S_l is the total spin of the shell.

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gThe interaction energy for symmetric and antisymmetric electron pairs with electrons belon|
*ing to the same shell is defined as $\langle s,t\,|1/r_{s,t}|\,s,t\rangle_{sym} = 2k_s\langle s\,|1/r_s|\,s\rangle$ and $\langle s,t\,|1/r_{s,t}|$
$s,t\rangle_{antisym} = (1-\varepsilon_s)2k_s\langle s\,|1/r_s|\,s\rangle$, respectively.

Similarly, expression $k_J (M-1)$, in Eq. (14b) and in Eq. (20b) must be replaced by

$$k_J \{(M-1) - \varepsilon_J ((3/4)(M-2) + S_J (S_J + 1)/M)\}. \qquad (22b)$$

In such a way a considerable amount of the exchange effect is rather well taken into account.

In Refs. 2 and 3 it was shown how parameters k_s, f_s and ε_s can be rather easily computed if we allow for a spherical averaging of the electron's wave function. It was also shown that they depend very little on Z, P and M. For higher n, l electrons they can be obtained using atomic ionization data. Very many experimental data can then be rather well reproduced, using a small set of even rather approximately determined parameters. Further, Fig. 2 indicates that $g_s = 0$ is a rather [good approximation at least for lower shells where the ratio r_t/r_s is high.

3. Quantitative analysis

In this section we shall make a quantitative comparison of the *IPM* with the Hartree-Fock, or experimental results. For the evaluation of the *IPM* data we shall use a set of parameters k_s, f_s and ε_s from Ref. 3, which is expected to represent average values for particular shells with an error of at most a few percent (taking also $g_s = 0$), except ε_s, which may carry a much larger error (20—50%). These constants are: $k_1 = 5/16$ (computed), $k_2 = 0.354$ (from ionization data analysis), $k_3 = 0.36$ (ioniz. data), $f_{2s} = 0.80$ (computed), $f_{2p} = 1.0$ (computed), $f_{3s} = 0.82$ (ioniz. data), $f_{3p} = 0.875$ (ioniz. data), $f_{3d} = 1.0$ (estimated), $\varepsilon_2 = 1/6$ (ioniz. data), $\varepsilon_3 = 0.1$ (ioniz. data). Corresponding parameters for individual electron pairs (see. (11a—b)) may deviate from these average values much more (up to about 20%). But the properties of individual electrons in an atom are defined by the average interaction with all other participating particles, so average values are important

Since we have split the single particle potential energy into its local part, which is represented by the individual particle potential energy $\langle W_{p,s} \rangle$, and into the nonlocal part $W_{p,s}^n$, it is worthwhile asking what is their relative amount. The ratio $W_{p,s}^0 / |\langle W_{p,s} \rangle|$ can be calculated in two rather independent ways. First we calculate $W_{p,s}^n$ as the difference between the Hartree-Fock single particle energy E_s and the independent particle energy W_s^0 (see Eqs. (20a—b)). Thus we find

$$R_s = \frac{W_{p,s}^n}{|\langle W_{p,s} \rangle|} = \frac{W_s^0 - E_s}{2W_s^0} = \left(1 - \frac{E_s}{W_s^0}\right)/2. \qquad (23)$$

(Instead of the Hartree-Fock single particle energy E_s one can also use experimetal electron removal energies $-E_s$). Values calculated in this way for $_7$N, $_{26}$Fe and $_{47}$Ag, as examples, are given in Table 1.

TABLE 1.

element	$W_{p,s}^n/|\langle W_{p,s} \rangle|$					
	$_7$N		$_{26}$Fe		$_{47}$Ag	
electron state	R_s	R_s'	R_s	R_s'	R_s	R_s'
1s	0.165	0.146	0.103	0.104	0.081	0.085
2s	0.283	0.298	0.244	0.211	0.201	0.221
2p	0.366	0.330	0.277	0.218	0.226	0.225
3s	—	—	0.300	0.405	0.286	0.325
3p	—	—	0.368	0.424	0.312	0.332
3d	—	—	0.476	0.473	0.364	0.337

The ratios of the nonlocal single particle potential energies to the local single particle potential energies $W_{p,s}^n/|\langle W_{p,s} \rangle|$ for various states in $_7$N, $_{26}$Fe and $_{47}$Ag : R_s as given by the ratio of the removal energy E_s versus single particle energy W_s^0 (see Eq. (23)), and R_s' as predicted by the IPM (see Eqs. (24a—b)).

Alternatively $W_{p,s}^n$ is given by the expression on the right hand side of Eq. (20a), or (20b). Dividing it by $|\langle W_{p,s}^0 \rangle| = Z^2/2n^2$ we find

$$R_i' = W_{p,i}^n/|\langle W_{p,i} \rangle| = (2/Z_i) [k_i (P - 1) + f_j M (n_i/n_j)^2 (Z_j/Z_i)] \qquad (24a)$$

$$R_j' = W_{p,j}^n/|\langle W_{p,j} \rangle| = (2/Z_j) k_j (M - 1) \qquad (24b)$$

for the lower and the upper shell electrons, respectively. (The extention to the case more than two shells is straightforward.)

An estimate of R_s' with g_s (and for $n < 3$) for $_7$N, $_{26}$Fe and $_{47}$Ag, as examples (also taking into account (22a—b)), are given in Table 1. Rather good agreement between the corresponding values of R_s and R_s' in Table 1 is an indication that the concept of nonlocal energy in the atom is meaningful. For $n > 3$, $g_s = 0$ is no longer a good approximation.

The nonlocal part of the single particle potential energy, assigned to a particular electron, is considerable. The limiting value is $R_s' = 0.5$ (for the case of positronium) and is rather well approached by external electrons.

Further comparison of the IPM with the Hartree-Fock model is made by calculating energy integrals (21a—e) and comparing them with Hartree-Fock data. Such a comparison for $_7$N and $_{26}$Fe, as examples, is given in Table 2. Hartree-Fock data were taken from Ref. 5, except the missing KE integrals for Fe, which were obtained from the relativistic $\langle 1/r \rangle_{HF}$ Hartree-Fock data of Ref. 6, using the relation $KE (s)_{HF} = Z_s \langle 1/r \rangle_{HF}/2$ and the virial theorem (18). Considering the rather approximately determined values of constants k, f and ε, the agreement is good for the lower state single particle integrals and less good for external electrons. It is also worth mentioning that in the IPM considered in Refs. 2 and 3 an average k is assumed for all electrons belonging to the same shell. So e. g. the disagreement observed in the $KE (3l)$ values is partly due to this average. If we average these $I (3l)$ values over all electrons within the third shell, we obtain average $I (3l)$ values, which agree quite well. Similar arguments also hold for the differences observed in the two particle energy integrals, where the agreement is less good, but

TABLE 2.

Slater integral	$_7$N		$_{26}$Fe	
	IPM	HF	IPM	HF
$KE(1s)$	44.89	44.27	659.88	667.45*
$KE(2s)$	4.32	4.46	123.08	124.56*
$KE(2p)$	3.53	3.72	118.69	118.37*
$KE(3s)$	—	—	18.20	22.23*
$KE(3p)$	—	—	16.68	19.47*
$KE(3d)$	—	—	13.44	13.44*
$I(1s)$	−48.91	−48.85	−675.93	−675.71
$I(2s)$	− 9.86	−10.60	−165.30	−165.38
$I(2p)$	− 9.35	− 9.64	−164.58	−164.05
$I(3s)$	—	—	− 55.75	− 63.28
$I(3p)$	—	—	− 54.09	− 59.55
$I(3d)$	—	—	− 50.10	− 44.49
$I(3l)$**	—	—	− 52.30	− 52.40
$F^0(1s, 1s)$	8.34	8.25	34.06	31.80
$F^0(1s, 2s)$	1.66	1.94	8.88	9.47
$F^0(1s, 2p)$	1.88	1.89	10.89	10.61
$F^0(2s, 2s)$	1.36	1.366	7.85	6.38
$F^0(2s, 2p)$	1.35	1.334	7.14	7.13
$F^0(2p, 2p)$	1.34	1.31	7.71	7.73
$F^0(3s, 3s)$	—	—	2.05	2.17
$F^0(3p, 3p)$	—	—	1.96	2.07
$F^0(3d, 3d)$	—	—	1.76	1.44

A comparison of energy integrals for $_{26}$Fe and $_7$N, as obtained by the IPM and HF[5] model. Values are given in Rydbergs (1 Ry = 13.6 eV).

still satisfactory. So the IPM essentially reproduces the basic atomic data nearly as well as the HF model.

4. Discussion

The IPM introduces the splitting of the potential energy operator into its local and nonlocal parts. In the central field approximation, by introducing the electron interaction constants k_s, screening constants g_s and f_s (and exchange interaction constants ε_s[3]) we are automatically led to hydrogen like independent particle solutions.

We may now make some remarks concerning the physical meaning of the various quantities which were introduced above.

The independent particle energies W_s^0 represent average negative removal energies of electrons belonging to a particular (sub)shell in sudden approximation. They differ from the single particle energies E_s, which represent to a good approxi-

*Deduced from $\langle 1/r \rangle$ values[6]

**$I(3l) = \sum_{l=1}^{3} (2l + 1) I(3l)/\Sigma(2l + 1)$

mation negative electron removal energies. The ratio R measures this difference (see Eqs. (23), (24a—b)). The difference between them $E_s - W_s^0 = W_{ps}^n$, as we have already mentioned above, represents the nonlocal part of the potential energy of s-th electron. The corresponding operator does not influence the shape of the wave function describing it.

The *IPM* reveals a specific sharing of the potential energy of interacting particles. But the sum of potential energies of all interacting electrons is simple. It may be written either in terms of matrix elements of local, or nonlocal potential energy operators:

$$\sum_{t>s}^{P+M-1} \sum_{s=1}^{P+M-1} \langle s, t \,|1/r_{s,t}|\, s, t \rangle = \sum_{s=1}^{P+M} \langle s \,|U_s(r_s)|\, s \rangle = \sum_{s=1}^{P+M} \sum_{t \neq s}^{P+M-1} \langle t \,|V_s(r_t)|\, t \rangle.$$

Similarly, the interaction energy of electrons with the atomic nucleus is

$$\sum_{t=1}^{P+M} \langle o, t \,|-Z/r_{0,t}|\, o, t \rangle = \sum_{t=1}^{P+M} \langle t \,|-Z/r_t|\, t \rangle = \sum_{t=1}^{P+M} \langle t \,|V_0(r_t)/\, t \rangle.$$

The total atomic nonlocal potential energy (including that of the atomic nucleus) is therefore equal to the local potential energy of all electrons.

That the nonlocal part of the potential energy operator does not influence a particular electron, can also be seen if we evaluate the force experienced by the s-th electron. The single particle potential energy operator is

$$W_s(r_s, r_t) = -Z/r_s + U_s(r_s) + \sum_{t \neq s} V_s(r_t) \tag{25}$$

and therefore

$$F_s(r_s) = -\partial W_s/\partial r_s = -Z/r_s^2 - dU_s(r_s)/dr_s.$$

If Eqs. (11a—c) were rigorously valid and if k_s, g_t and f_j were constants, explicitely independent of r_s, or r_t, then $U_s(r_s)$ would be proportional to $1/r_s$ and

$$F_s(r_s) = -Z_s/r_s^2.$$

Then also the virial theorem (18) would hold exactly. The above mentioned assumptions were already partly discussed in Refs. 2 and 3 and are further analyzed in the Appendix. Such an analysis indicates that these assumptions are rather well satisfied for most atoms.

How well does the virial theorem (18) hold? Its validity can be estimated if we approximate the local single particle potential energy operator by an operator which deviates from the Coulomb-like one, namely

$$W_p'(r_s) = -Z_s/r \qquad . \tag{26}$$

Then the following virial theorem would hold for individual electrons

$$2 \langle W_{k,s} \rangle + (1 + \gamma_s) \langle W'_{p,s} \rangle = 0. \tag{27}$$

But because (19) should be exactly valid simultaneously, it also follows that

$$\sum_{=1}^{P+M} \gamma_s \langle W'_{p,s} \rangle = 0.$$

So the correction factors γ_i and γ_j must be of opposite sign. For the simplified atom, described in Fig. 1, we have

$$\gamma_i / \gamma_j = - n_i^2 M Z_j^2 / n_j^2 P Z_i^2. \tag{28}$$

If the *IPM* predicts $\gamma_s = 0$, what correction factors γ_s are predicted by the Hartree-Fock model? Using (27) and (21a—b), we find

$$(1 + \gamma_s) = (2Z/Z_s) (KE(s)_{HF} / PE(s)_{HF})$$

where $KE(s)_{HF}$ and $PE(s)_{HF}$ are the corresponding Hartree-Fock values, while Z_s are defined by (14a, b), or better by (22a). Using Hartree-Fock data from Table 2 for $_7$N and rather approximate values for k_s, f_s and ε_s, which determine Z_s, we find γ_s values as given in Table 3.

TABLE 3.

$1 + \gamma \, 1s = 1 - 0.005$
$1 + \gamma \, 2s = 1 + 0.005$
$1 + \gamma \, 2p = 1 + 0.030$

Correction factors γ_s, describing the deviations of the potential energy operator from the Coulomb-like potential, for the Hartree-Fock model for ^{7}N.

Correction factors γ_s are obviously small even for such light atoms as $_7$N. Also Eq. (28) is rather well obeyed, especially if one recalls the uncertainties carried by Z_{2s} and Z_{2p} due to the rather approximately known parameters k_2, f_{2s} and ε_2.

According to the *IPM*, the nonlocal part of the single particle potential energy operator does not influence the single particle wave function Ψ_s, describing a particular electron. Or vice versa: that part of the single particle potential energy operator, which does not influence the single particle wave function, is defined as nonlocal. For example, let us consider the simplified atom in Fig. 1. The removal of the upper shell electrons in the *IPM* does not disturb the lower shell electrons if $g_i = 0$. For non-overlapping shells this statement is obviously correct. Inspection of Fig. 2 also indicates that $g_s = 0$ is often a good approximation. The same conclusion can be drawn from Table 3 for the $1s$ and $2s$ states in $_7$N.

The removal of the lower shell electrons does, however, influence the wave functions of the lower and the upper shell electrons considerably. However, the *IPM* predicts the constant screening experienced by the upper shell electrons due to the presence of the lower shell electrons: $\chi_J = Z_J/Z$, which contradicts (3). Within the *IPM* such in approximation is rather well justified, as might be qualitatively understood according to the following reasoning: Let us replace a single particle potential energy operator, describing the upper shell electron of Fig. 1, by a slightly more general one, namely by

$$W_{p,J}(r_J) = -Z_J/r_J - a/r_J^\alpha + b/r_J^\beta. \tag{29}$$

The physical meaning of the two correction terms added to the Coulomb like potential is the following:

The attractive term $-a/r_J$ $(a > 0; \alpha > 1)$ expresses the fact that the j-th electron belonging to the upper shell experiences the increased central charge when it penetrates into the region of the lower shell. The range of this term is approximately equal to the radius r_l of the lower shell.

The repulsive term b/r_J $(b > 0; \beta > 1)$ approximates the repulsion of the lower shell electrons due to the Pauli principle. The two electrons having parallel spins and approaching each other in their centre of mass system with opposite momenta $p = \hbar k$ behave as elastic spheres with diameter $2r_c = \dfrac{1}{k} \approx \dfrac{r_l}{n_l}$ [3]. Therefore the range of this term is approximately $r_c = r_l/n_l$. The virial theorem for the particle moving in the potential (29) then is

$$\langle 2W'_{k,J}\rangle = \langle +r_J \frac{\mathrm{d}W'_{p,J}}{\mathrm{d}r_J}\rangle = +\langle \frac{Z_J}{r_J}\rangle + \langle \frac{a}{r_J}\rangle - \langle \frac{b}{r_J}\rangle. \tag{30}$$

The correction terms added to the $\langle Z_J/r_J\rangle$ are not only small when compared with $\langle Z_J/r_J\rangle$, but also of opposite sign. This expression is equal to (18) only if the last two terms of equation (30) cancel out. But even if they do not cancel completely, partial cancelation leads to a Coulomb like potential Z_J/r with a short range correction potential added, the range and the strength of this correction potential being much smaller than the strength and ranges of separate correction terms in (29). The repulsive potential produced by the Pauli principle therefore inhibits the increase of the screening function $\chi_J(r_J)$ when r_J approaches zero.

So the validity of the virial theorem (18) is at least partly based on the validity of the Pauli principle. The reduced screening experienced by the upper shell electron in the region of the lower shell is compensated by the repulsion due to the Pauli principle.

5. Conclusion

Splitting the single particle potential energy operator into its local and nonlocal term, together with the assumption that k_s, g_l and f_J are independent of $\langle r_s \rangle$, leads in the central field approximation to hydrogen-like individual particle states.

Even within a very simplified version of the atomic model, where the same electron interaction constant k_s is taken for all electrons belonging to the same shell, and the same screening constant f_s is taken for electrons of a given subshell (and the same exchange interaction constant ε_s for electron pairs belonging to the same shell), many atomic data are reproduced nearly as well as with the much more elaborate Hartree model (and comparably as well as the Hartree-Fock model).

Therefore, one is tempted to pose the following question: how exactly does the virial theorem (18) hold in the many electron atom? Or, can Eq. (18) be the defining equation for the (local part of the) single particle potential energy $\langle W_{p,s} \rangle$? A more thorough analysis of the *IPM* might yield an answer.

6. Appendix

The virial theorem (19) must be generally valid for the true atom. It is not expected to be valid for approximate atomic models. (Surprisingly, it is valid for the Thomas-Fermi model). Its validity is well known to be intimately related with atomic scaling relations. But the separate validity of the virial theorem (18) for individual electrons is a property of hydrogenic atomic models. However, conventional hydrogenic models do not obey the virial theorem (19) for the whole atom. The *IPM* satisfies both conditions. This is equivalent to the statement that electron interaction constants k_s and the screening constants g_s and f_s (disregarding other effects, such as the exchange interaction) do not depend on the variation of the average radii of either of the individual shells. How well is such a condition fulfilled?

The electron interaction constant k_s is defined as the ratio of the average inverse distance of the two electrons belonging to the same shell and the inverse radius of the shell[3]. For electrons described by spherically averaged hydrogen--like wave functions k_s is therefore obviously independent on the shrinking or the expansion of either of the shells.

To estimate the dependence of the screening parameters g_s and f_s on the variation of radii of the corresponding shells, we first calculate the analytical expression for g_t and f_t for simplified electron distributions of interacting electrons.

We assume uniform charge distributions of interacting s- and t-electrons up to maximum radii r_s and r_t, respectively

$$\varrho_s = \begin{cases} A_s \text{ for } r < r_s \\ 0 \quad \text{for } r > r_s \end{cases}$$

$$\varrho_t = \begin{cases} A_t \text{ for } r > r_t \\ 0 \quad \text{for } r < r_t. \end{cases}$$

Then we split the potential energy $W_p = \langle s, t \,|1/r_{s,t}|\, s, t \rangle$ into two parts:

$$W_p = \int\limits_0^{r_s} \varphi_s(r)\, dq_t + \int\limits_{r_s}^{r_t} \varphi_s(r)\, dq_t.$$

The first part of the potential energy

$$\int_0^{r_s} \varphi_s(r)\, dq_t = (4/5)\, \langle 1/r_s \rangle\, \beta$$

where $\langle 1/r_s \rangle = \langle s\,|1/r_s|\,s \rangle = 3/2r_s$ and $\beta = (r_t/r_s)^{-3}$, is shared equally by both electrons. The second part

$$\int_{r_s}^{r_t} \varphi_s(r)\, dq_t = (1 - \beta^{2/3})\, \langle 1/r_t \rangle$$

with $\langle 1/r_t \rangle = \langle t\,|1/r_t|\,t \rangle = 3/2r_t$ is the local potential energy of the external electron only. Therefore

$$W_p = (2/5)\, \beta\, \langle 1/r_s \rangle + \left(1 - \beta^{2/3} + (2/5)\, \beta\, \frac{1/r_s}{1/r_t}\right) \langle 1/r_t \rangle.$$

By comparison with Eq. (10) we find

$$g_s = (2/5)/(r_t/r_s)^3 \qquad f_t = 1 - (3/2)/(r_t/r_s)^2.$$

For $r_s = r_t$ we find $g_s = f_t = k_s = 2/5$. The dependence of f_t and g_s on r_t/r is given in Fig. 2. As long as $\langle 1/r_s \rangle / \langle 1/r_t \rangle > 2$ (and this condition is often very well satisfied), the approximation $g_s = 0$ is justified.

For fully nonoverlapping shells, $f_t = 1$ and $g_s = 0$ and the virial theorems (18) and (19) hold exactly. Such an approximation is rather good for electron pairs with $(n_t - n_s) > 2$ and even for electron pairs with $(n_t - n_s) = 2$ and with $l_t = n_t - 1$ (as e. g. for 1s ad 2p electron pair).

Since the ratio $\langle 1/r_s \rangle / \langle 1/r_t \rangle$ is only slightly changed in most atomic processes (e. g. if we add to or remove one electron from either of the shells), screening parameters g_s and f_t are approximately constant, due to low value of the derivative $df_t/d\,(r_t/r_s)$ (and $dg_s/d\,(r_t/r_s)$) in the region of interest.

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O ATOMSKIH MODELIH S CENTRALNIM POLJEM

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Sklopitvi enodelčnih Schrödingerjevih enačb, ki popisujejo posamezne elektrone v modelu Hartree-Focka, se izognemo s preprosto redefinicijo enodelčne potencialne energije elektrona, ki omogoča da popišemo elektron kot sistem neodvisnih kvazi-delcev, za katere velja enak virialni teorem kot za atome.