$X\alpha$ Method with Pseudopotentials

Levente Szasz
Department of Physics, Fordham University, New York

Z. Naturforsch. **35a**, 628–636 (1980); received April 20, 1980

The $X\alpha$ method for an atom or molecule is transformed into an all-electron pseudopotential formalism. The equations of the $X\alpha$ method are exactly transformed into pseudo-orbital equations and the resulting pseudopotentials are replaced by simple density-dependent potentials derived from Thomas-Fermi model. It is shown that the new formalism satisfies the virial theorem. As the first application it is shown that the model explains the shell-structure of atoms by the property that the pseudo-orbitals for the $(n\mathrm{s})$, $(n\mathrm{p})$, $(n\mathrm{d})$ etc. electrons are, in a very good approximation, the solutions of the same equation and have their maxima at the same point thereby creating the peaks in the radial density characterizing the shell structure.

I. Introduction and Summary

It is well known that the replacement of the exchange interaction terms in the Hartree-Fock equations by a density-dependent potential derived from the Thomas-Fermi model presents an attractive computational simplification. This model, called the "$X\alpha$ approximation" was developed by several scientists and culminated in the work of Slater [1].

The purpose of this paper is to show that the $X\alpha$ method can be further simplified by the introduction of pseudopotentials replaceing the orthogonality requirement between the one-electron orbitals. Here we shall make use of a new development in pseudopotential theory which is being presented by the author in a series of papers [2, 3]. The main feature of this new development is that while previously the pseudopotential theory was developed for one [4–9] or more [10–13] valence electrons, in the work of the author [2, 3] the theory is applied to all electrons of an atom or molecule. Specifically we have formulated an all-electron pseudopotential model [3] (APM) which was first applied to the calculation of the average-of-configuration energies of atoms between Li and Kr. In these calculations a single Slater function was used for every pseudo-orbital and excellent results were obtained for the total energies and total radial densities [3]. The present paper relies on the techniques developed in connection with the APM.

We start in Sect. II by transforming the $X\alpha$ equations for an atom or molecule *exactly* into pseudo-orbital equations by using the transformation techniques developed by the author which are applicable to all electrons (not only valence). Since the exact pseudopotential operator which appears in these equations is a rather complicated expression, in Sect. III, we approximate it by simple, density-dependent local pseudopotentials which are derived using the Thomas-Fermi model. We present two different but equivalent pseudopotentials, one depending on densities and applicable to molecules the other depending on radial densities and applicable only to atoms with spherical symmetry. In Sect. IV we show that the new formalism satisfies the virial theorem. In Sect. V we present the first application of the model which consists of showing that it predicts the shell structure of atoms. This will be done by proving that in the pseudopotential model an electron with quantum numbers n and l moves in a effective potential which is, in a very good approximation, l-independent i.e. it depends only on the principal quantum number n. This means that in a very good approximation the (ns), (np), (nd) etc. pseudo-orbitals will have their maxima at the same point thereby creating the peaks in the total radial density characterizing the shell-structure.

II. Exact Transformation of the $X\alpha$ Equations into Pseudopotential Equations

First we formulate here the $X\alpha$ model for an atom or molecule. Let ϱ be the total electron den-

---

Reprint requests to Dr. L. Szasz, Department of Physics, Fordham University, New York N. Y. 10458, U.S.A.

0340-4811 / 80 / 0600-0628 $ 01.00/0. — Please order a reprint rather than making your own copy.

sity (we do not define separate densities for up and down spin) defined in terms of N spin-orbitals $\varphi_1 \ldots \ldots \varphi_N$:

$$\varrho = \sum_{i=1}^{N} |\varphi_i|^2 . \tag{2.1}$$

The total energy of the system in the $X\alpha$ model is given as

$$E_{\mathrm{T}} = \sum_{i=1}^{N} \int \varphi_i^* (t + g) \varphi_i \, \mathrm{d}q + \tfrac{1}{2} \int \varrho V_{\mathrm{c}} \mathrm{d}q - \alpha \int \varrho^{4/3} \mathrm{d}q , \tag{2.2}$$

where t is the kinetic energy operator, g is the potential of the nucleus/nuclei, V_{c} is the electrostatic potential of all electrons and the last term is the exchange interaction energy with the adjustable parameter α. Variation of E_{T} gives the $X\alpha$ equations:

$$H_{X\alpha} \varphi_i = \varepsilon_i \varphi_i , \quad (i = 1, \ldots, N) , \tag{2.3}$$

where $H_{X\alpha}$ is the Hamiltonian:

$$H_{X\alpha} = t + V_{X\alpha} , \tag{2.4}$$

with the $X\alpha$ potential being given as

$$V_{X\alpha} = g + V_{\mathrm{c}} - \tfrac{4}{3} \alpha \varrho^{1/3} . \tag{2.5}$$

[Since the total energy (2.2) depends only on the first order density matrix plus the total density which are invariant under a unitary transformation we do not get off-diagonal Lagrangian multipliers into (2.3).] The solutions of (2.3) are orthonormal:

$$\langle \varphi_i | \varphi_k \rangle = \delta_{ik} , \tag{2.6}$$

and ϱ is normalized to N:

$$\int \varrho \, \mathrm{d}v = N . \tag{2.7}$$

Let ψ_i be a pseudowavefunction formed from the given $X\alpha$ orbitals with arbitrary α_{ik} parameters:

$$\psi_i = \varphi_i + \sum_{k=1}^{i-1} \alpha_{ik} \varphi_k , \tag{2.8}$$

and consider the pseudopotential [3]

$$V_i = \Omega_i (\varepsilon_i - V_{X\alpha} - E_k{}^i) - (1 - \Omega_i)(H_{X\alpha} - \varepsilon_i) \Omega_i . \tag{2.9}$$

In this operator $H_{X\alpha}$, $V_{X\alpha}$ and ε_i are the $X\alpha$ hamiltonian, potential and orbital parameter respectively and

$$\Omega_i f = \sum_{k=1}^{i-1} \varphi_k(1) \int \varphi_k^*(2) f(2) \, \mathrm{d}q_2 \tag{2.10}$$

is a projection operator onto the orbitals $\varphi_1 \ldots \varphi_{i-1}$ and

$$E_k{}^i = \frac{\langle \psi_i | t | \psi_i \rangle}{\langle \psi_i | \psi_i \rangle} \tag{2.11}$$

is the expectation value of the kinetic energy with respect to the pseudo-orbital (2.8).

Now consider

$$(H_{X\alpha} + V_i) \psi_i = \varepsilon_i \psi_i , \quad (i = 1, 2, \ldots, N) . \tag{2.12}$$

As we have shown in a recent publication [3] in which we have transformed the Hartree-Fock equations for an arbitrary configuration into pseudopotential equations, the Eqs. (2.12) with V_i defined by (2.9) have the following properties:

(1) The equations possess a set of solutions of the form of (2.8) with *uniquely defined* parameters α_{ik}. The α_{ik} are determined in such a way that the kinetic energy (2.11) is a minimum for each pseudo-orbital ψ_i.

(2) The solutions of the $X\alpha$ equations (2.3), the orbitals φ_i and the orbital parameters ε_i are exactly reproduced by (2.12) meaning that the orbital parameters in (2.12) are equal to the orbital parameters in (2.3) and the pseudo-orbitals ψ_i reproduce the $X\alpha$ orbitals φ_i through the Equation (2.8).

The pseudopotential (2.9) is the most general for a set of one-electron equations. If all electrons are moving in the same potential, which is the case in the $X\alpha$ model, then (2.9) can be simplified. We have

$$\Omega_i H_{X\alpha} = H_{X\alpha} \Omega_i \tag{2.13}$$

and

$$(1 - \Omega_i) \Omega_i = \Omega_i - \Omega_i{}^2 = 0 . \tag{2.14}$$

Therefore the last term in (2.9) is zero and we get

$$V_i = \Omega_i (\varepsilon_i - V_{X\alpha} - E_k{}^i) . \tag{2.15}$$

Changing this into a local potential we put

$$\Phi_i = V_i \psi_i / \psi_i , \tag{2.16}$$

and our Eqs. (2.12) become

$$(H_{X\alpha} + \Phi_i) \psi_i = \varepsilon_i \psi_i , \quad (i = 1, \ldots, N) . \tag{2.17}$$

We introduce now the pseudo-orbitals into the total energy expression. From (2.3) we obtain:

$$\sum_{i=1}^{N}\varepsilon_i = \sum_{i=1}^{N}\langle\varphi_i|\,H_{X\alpha}\,|\varphi_i\rangle = \sum_{i=1}^{N}\langle\varphi_i|\,t+V_{X\alpha}\,|\varphi_i\rangle\,. \tag{2.18}$$

Let us define a functional of all $X\alpha$ orbitals as

$$E_0[\varphi_i] = E_{\mathrm{T}} - \sum_{i=1}^{N}\langle\varphi_i|\,H_{X\alpha}\,|\varphi_i\rangle = E_{\mathrm{T}} - \sum_{i=1}^{N}\langle\varphi_i|\,t+V_{X\alpha}\,|\varphi_i\rangle\,. \tag{2.19}$$

Using (18) we get

$$E_{\mathrm{T}} = E_0[\varphi_i] + \sum_{i=1}^{N}\varepsilon_i\,. \tag{2.20}$$

It is easy to see that

$$E_0[\varphi_i] = -\tfrac{1}{2}\int\varrho\,V_{\mathrm{c}}\,\mathrm{d}v + \tfrac{1}{3}\alpha\int\varrho^{4/3}\,\mathrm{d}v\,. \tag{2.21}$$

From (2.17) we obtain

$$\sum_{i=1}^{N}\varepsilon_i = \sum_{i=1}^{N}\langle\psi_i|\,H_{X\alpha}+\Phi_i\,|\psi_i\rangle\,. \tag{2.22}$$

On putting (2.22) into (2.20) we get the total energy in a form which contains the pseudo-orbitals and pseudopotentials:

$$E_{\mathrm{T}} = E_0[\varphi_i] + \sum_{i=1}^{N}\langle\psi_i|\,H_{X\alpha}\,|\psi_i\rangle + \sum_{i=1}^{N}\langle\psi_i|\,\Phi_i\,|\psi_i\rangle\,. \tag{2.23}$$

We note that this expression still contains the orthogonal $X\alpha$ orbitals, since, as we see from (2.21) the $E_0[\varphi_i]$ is given in terms of these and it is clear from the derivation that the potentials in $H_{X\alpha}$ as well as in Φ_i are given in terms of the φ_i. To compare (2.23) with the original $X\alpha$ total energy we write down here (2.20) again with ε_i replaced according to (2.18):

$$E_{\mathrm{T}} = E_0[\varphi_i] + \sum_{i=1}^{N}\langle\varphi_i|\,H_{X\alpha}\,|\varphi_i\rangle\,. \tag{2.24}$$

We have now two equivalent procedures for the calculation of atomic or molecular properties in the $X\alpha$ approximation. The "conventional" $X\alpha$ procedure consist of solving Eqs. (2.3), obtaining the orthonormal orbitals $\varphi_1 \ldots \varphi_N$ and getting the total energy from (2.24). The new procedure presented here consist of solving the pseudopotential epuations (2.15) — (2.17), obtaining the pseudo-orbitals

$$\psi_1 \ldots \psi_N$$

and getting the total energy from (2.23). This last expression still contains the orbitals φ_i; therefore these must be computed from the pseudo-orbitals by Schmidt-orthogonalization according to (2.8). Since the transformation is exact the two procedures are completely equivalent (the introduction of pseudo-orbitals does not *a priori* mean an approximation).

III. Density-Dependent Pseudopotentials

The exact pseudopotential (2.15) is a fairly complicated operator. We shall show here that it can be transformed into simple, density-dependent potentials by means of the Thomas-Fermi model. The transformation will rest on the assumption that, the energy resulting from the pseudopotential, which replaces the Pauli exclusion principle with respect to lower lying orbitals, is a purely kinetic energy. Let $\hat{\gamma}_i$ be the Thomas-Fermi kinetic energy which is necessary to raise the electron into the orbital φ_i i.e. let $\hat{\gamma}_i$ be the kinetic energy in the orthogonalized state φ_i. Let γ_i be the same in the non-orthogonal state ψ_i (γ_i will be called the "kinetic self-energy"). Then we state that the pseudopotential Φ_i in Eq. (2.17) can be replaced by

$$\Phi_i = \hat{\gamma}_i - \gamma_i\,. \tag{3.1}$$

Physical plausibility would require only the first term. It is easy to see however that γ_i must be substracted. Put (3.1) into (2.17), multiply from left by $\psi_i{}^*$ and integrate. Then we get for the expectation value of the kinetic energy of the i-th orbital

$$\langle E_k{}^i\rangle = \langle\psi_i|\,t\,|\psi_i\rangle + \langle\psi_i|\,\gamma_i\,|\psi_i\rangle - \langle\psi_i|\,\gamma_i\,|\psi_i\rangle\,. \tag{3.2}$$

Now if we extract the kinetic energy of the orthogonal orbital from (2.3) we obtain

$$\langle\hat{E}_k{}^i\rangle = \langle\varphi_i|\,t\,|\varphi_i\rangle\,. \tag{3.3}$$

If $\hat{\gamma}_i$ and γ_i are accurately representing what they should according to the definition above then

$$\langle\psi_i|\,\gamma_i\,|\psi_i\rangle \approx \langle\psi_i|\,t\,|\psi_i\rangle\,,$$

and

$$\langle E_k{}^i\rangle \approx \langle\psi_i|\,\hat{\gamma}_i\,|\psi_i\rangle \approx \langle\varphi_i|\,t\,|\varphi_i\rangle = \langle\hat{E}_k{}^i\rangle\,, \tag{3.4}$$

i.e. the expression (3.1) is constructed in such a way that the total kinetic energy of the pseudo-orbital be approximately equal to the kinetic energy of the orthogonal $X\alpha$ orbital φ_i.

Now let the radius of the Fermi sphere containing the electrons up to and including φ_i be p and let p_ε be the "momentum width" associated with the self-energy of the orbital ψ_i. We put

$$\hat{\gamma}_i = p^2/2\,m\,, \tag{3.5}$$

and

$$\gamma_i = p_\varepsilon{}^2/2\,m\,. \tag{3.6}$$

On putting (3.5) and (3.6) into (3.1) we get

$$\Phi_i = \frac{1}{2\,m}\,(p^2 - p_\varepsilon{}^2)\,. \tag{3.7}$$

This is the basic expression for the pseudopotential but it must be refined by recalling that in an atom or molecule φ_i has definite symmetry. Let us assume that the system is such that the lowest orbitals $\varphi_1 \ldots \varphi_m$ are of different symmetry from φ_i, which means that φ_i will be orthogonal to these orbitals:

$$\langle \varphi_i \,|\, \varphi_l \rangle = 0\,, \qquad (l = 1, \ldots, m;\; i = m+1, \ldots, N)\,. \tag{3.8}$$

Translating this into the language of the Thomas-Fermi model we define p_{00} to be the radius of the Fermi sphere filled by $\varphi_1 \ldots \varphi_m$. The orthogonalization energy of the orbital φ_i will not be $\hat{\gamma}_i$ but only $(\hat{\gamma}_i - p_{00}^2/2m)$. Likewise let us assume that the orbitals immediately below φ_i are orthogonal to φ_i by symmetry. Let these orbitals be $\varphi_{i-1}, \varphi_{i-2}, \ldots \varphi_{s+1}$ i.e. the highest orbital to which φ_i must be orthogonalized is φ_s. Let p_0 be the Fermi sphere up to and including φ_s. Then we can exclude $(\varphi_{s+1}, \ldots, \varphi_{i-1})$ as well as obtain a meaningful definition for p_ε if we redefine p as

$$p = p_0 + p_\varepsilon; \quad p_\varepsilon = p - p_0\,. \tag{3.9}$$

With these modifications we obtain

$$\begin{aligned} \Phi_i &= \frac{1}{2\,m}\,(p^2 - p_\varepsilon{}^2 - p_{00}^2) \\ &= \frac{1}{2\,m}\,(p_0{}^2 + 2\,p_0\,p_\varepsilon - p_{00}^2)\,. \end{aligned} \tag{3.10}$$

We transform this into a density-dependent potential using the Fermi relationship

$$p_{\mathrm{F}} = (3\,\pi^2)^{1/3}\,\varrho^{1/3}\,. \tag{3.11}$$

Let

$$\varrho_0 = \sum_{k=1}^{s} |\,\varphi_k\,|^2\,, \tag{3.12}$$

$$\varrho_{00} = \sum_{k=1}^{m} |\,\varphi_k\,|^2\,, \tag{3.13}$$

and

$$\varrho = \varrho_0 + |\,\varphi_i\,|^2\,. \tag{3.14}$$

In these formulas ϱ_0 is the density up to and including φ_s, ϱ_{00} is the same up to and including φ_m and ϱ is defined in accordance with (3.9). Using (3.11) for p, p_0 and p_{00} we get from the first line of (3.10)

$$\Phi_i = \tfrac{1}{2}\,(3\,\pi^2)^{2/3} \cdot [\varrho^{2/3} - \varrho_{00}^{2/3} - (\varrho^{1/3} - \varrho_0{}^{1/3})^2]\,. \tag{3.15}$$

It is evident from the derivation that the main term is the first; the second term usually contains only few electrons and is much smaller; the last term is the self-energy, which is again, by definition, much smaller than the first.

Restricting now the discussion to *atoms*, we divide the kinetic energy into radial and azimuthal parts according to Fermi [14]. Let p_{r} be the radial component and p_φ be the azimuthal component of the Fermi momentum (see Figure 1). As we see from the Figure, the following relationship holds

$$\frac{p_{\mathrm{F}}{}^2}{2\,m} = \frac{p_{\mathrm{r}}{}^2}{2\,m} + \frac{p_\varphi{}^2}{2\,m}\,, \tag{3.16}$$

where p_{F} is the radius of the Fermi sphere. For p_φ Fermi suggested [14] an expression and for p_{r} Gom-

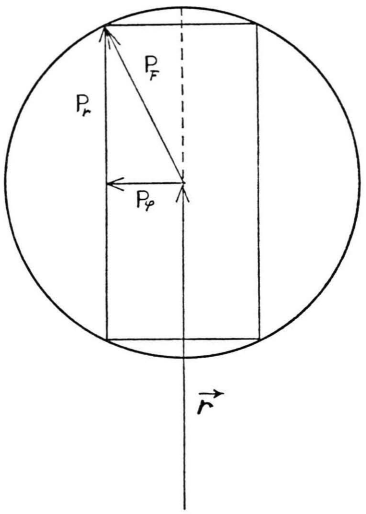

Fig. 1. The subdivision of the momentum space according to Fermi. Placed at the tip of the position vector $\boldsymbol{r}$ we have the Fermi sphere with the radius p_{F}. The radial and azimuthal components of p_{F} are p_{r} and p_φ.

bas derived one [15]. These are, in atomic units

$$p_\varphi = (l + \tfrac{1}{2})\,1/r\,, \tag{3.17}$$

and

$$p_\mathrm{r} = \frac{\pi}{2}\,\frac{D_l}{(2l+1)}\,. \tag{3.18}$$

In these expressions l is the azimuthal quantum number and D_l is the radial density of all electrons which have the azimuthal quantum number l among those which fill the Fermi sphere p_F.

Now let the principal and azimuthal quantum numbers of the $X\alpha$ state φ_i be n and l. Then, by definition, the states $s+1, s+2, \ldots, i-1$ are those in the same shell with φ_i i.e. φ_s becomes the highest energy state of the shell with the principal quantum number $(n-1)$. Identifying p_F with p and using (3.16), (3.17) and (3.18) we obtain for the first term of (3.15):

$$\frac{p^2}{2m} = \frac{1}{2}(3\pi^2)^{2/3}\varrho^{2/3} = \frac{\pi^2}{8}\,\frac{\hat{D}_l{}^2}{(2l+1)^2} + \frac{(l+\frac{1}{2})^2}{2r^2}\,, \tag{3.19}$$

where

$$\hat{D}_l = \sum_{n'=1}^{n-1} P_{n'l}^2\, q(n'l) + P_{nl}^2\,, \tag{3.20}$$

[$q(n'l)$ is the occupation number of the state $(n'l)$].

For the second term in (3.15) we recall that this was introduced because the lowest m orbitals were orthogonal to φ_i by their symmetry; in the case of atoms this means that the azimuthal quantum number of the orbital φ_i is different from the azimuthal quantum numbers of $\varphi_1 \ldots \varphi_m$. The orthogonalization energy is then purely azimuthal and we replace the $\varrho_{00}^{2/3}$ term by $(l+\frac{1}{2})^2/2r^2$. Finally, for the last term of (3.15) which is the self-energy, we go back to (3.9) and replace that relationship by

$$p_{\varepsilon\mathrm{r}} = p_\mathrm{r} - p_{0\mathrm{r}}\,, \tag{3.21}$$

where p_r and $p_{0\mathrm{r}}$ are the maximum radial momenta associated with the Fermi momenta p and p_0. We see from (3.16) and (3.17) that this is a meaningful step since the azimuthal momenta associated with p and p_0 are the same and cancel out approximately from the difference $(p-p_0)$, leaving (3.21).

Using (3.19) and (3.20) for the first term of (3.15), the azimuthal expression $(l+\frac{1}{2})/2r^2$ for the second term and (3.21) with (3.18) for the self-energy we obtain finally the pseudopotential

$$\Phi_{nl} = \frac{\pi^2}{8(2l+1)^2}\,[D_l{}^2 + 2\,D_l P_{nl}^2]\,, \tag{3.22}$$

where we have replaced the i index by (nl) and

$$D_l = \sum_{n'=1}^{n-1} P_{n'l}^2\, q(n'l)\,. \tag{3.23}$$

Summing up our results up to this point we recal that our pseudopotential equations (2.17) are

$$(H_{X\alpha} + \Phi_i)\,\psi_i = \varepsilon_i\,\psi_i\,, \qquad (i = 1, \ldots, N)\,, \tag{3.24}$$

which are exactly equivalent to the $X\alpha$ Eqs. (2.3) with the pseudopotential (2.15). We now replace (2.15) by the simple, density-dependent pseudopotentials (3.15) or (3.22). In deriving these we made two approximations. First, we replaced (2.15) by (3.1) and then we transformed (3.1) using the Thomas-Fermi model. In order to compensate for these approximations, at least partially, we multiply (3.15) and (3.22) by an adjustable parameter η so that our pseudopotentials finally become,

(1) for an arbitrary system i.e. for an atom or molecule:

$$\Phi_i = \eta\,\tfrac{1}{2}(3\pi^2)^{2/3} \cdot [\varrho^{2/3} - \varrho_{00}^{2/3} - (\varrho^{1/3} - \varrho_0{}^{1/3})^2]\,; \tag{3.25}$$

(2) for an atom with spherical symmetry:

$$\Phi_{nl} = \eta\,\frac{\pi^2}{8(2l+1)^2}\,[D_l{}^2 + 2\,D_l P_{nl}^2]\,. \tag{3.26}$$

We obtain our pseudopotential model by putting either (3.25) or (3.26) into (3.24) and then computing the total energy of the system from (2.23). As the last step we introduce now an approximation which we first introduced in the APM model and which we called the "pseudo-orbital condition" [3]. From (2.23) we see that E_T still contains the orthogonalized orbitals φ_i. It is clear however that the total energy does not depend explicitely on these orbitals but only implicitely through the total density ϱ and through partial densities which are in the pseudopotentials. The pseudo-orbital condition is an approximation by which we replace everywhere the φ_i by the pseudo-orbitals ψ_i, which, in this case means replacing the densities formed from the φ_i by the densities formed from the ψ_i. All potentials and the energy expression (2.23) retain their functional form but the φ_i disappear from the model which becomes a pseudo-orbital model exclusively.

We note that the pseudo-orbital condition has been very successful in the all-electron single-Zeta calculations based on the APM model in which, instead of the $X\alpha$ approximation, the average-of-configuration formula of Slater was used [3]. Since in the $X\alpha$ model all quantities depend on the densities rather then on the individual orbitals as in Slater's average-of-configuration approach the pseudo-orbital condition, which gave very good results for the densities, should work in the $X\alpha$ model as well.

The connection of our density-dependent pseudopotentials to previously developed formulas is as follows. For the valence electrons of atoms Gombas developed several formulas for density-dependent pseudopotentials [16]. The potential (3.25) was derived by Gombas for valence electrons and tested in calculations [16], [17] (without the self-energy term). Gombas also derived [15] a potential similar to (3.26); in the form presented here the potential (3.26) was first derived by the author in connection with the APM model [3] and has given excellent results for the total energies and total densities of atoms from Li to Kr. Therefore both (3.25) and (3.26) were tested in various atomic calculations; there is every reason to believe that the model will be successful in molecular calculations as well.

The main difference between Gombas' and our work must be emphasized. While the earlier derivations were always for valence electrons the author's work is an all-electron model; also, through Eq. (3.1) our presentation is tied to the exact pseudopotential transformation which was presented in the preceding Section.

IV. The Virial Theorem

Slater has shown [1] that the $X\alpha$ model satisfies the virial theorem for an arbitrary choice of α. We will show here that the $X\alpha$ model with the pseudopotentials (3.25) or (3.26) satisfies the virial theorem for an arbitrary choice of η.

We use the method of scaling developed by Fock [18]. Let $\psi_1 \ldots \psi_N$ be the solutions of (3.24) with either (3.25) or (3.26), and let us introduce the scale factor λ as a variational parameter. The "scaled" pseudo-orbitals will be

$$\psi_i{}^\lambda = \lambda^{3/2}\psi_i(\lambda\boldsymbol{r}), \quad (i = 1, \ldots, N), \tag{4.1}$$

and the scaled densities are

$$\begin{aligned} \varrho^\lambda &= \lambda^3\varrho(\lambda\boldsymbol{r}), \\ \varrho_0{}^\lambda &= \lambda^3\varrho_0(\lambda\boldsymbol{r}), \\ \varrho_{00}^\lambda &= \lambda^3\varrho_{00}(\lambda\boldsymbol{r}), \end{aligned} \tag{4.2}$$

where the λ factors insure that the scaled quantities are normalized in the same way as the unscaled. The expression for the total energy is given by (2.23) and it is evident from a comparison with (2.24) that the first two terms of (2.23) correspond to the original $X\alpha$ energy expression; let E_k and E_p be the kinetic and potential energy parts of that expression. Let $E_k{}^\lambda$ and $E_p{}^\lambda$ be the corresponding scaled quantities and let

$$E_\mathrm{D} = \sum_{i=1}^{N} \int \psi_i{}^* \Phi_i \psi_i \,\mathrm{d}v \tag{4.3}$$

be the pseudopotential term in (2.23), and E_D^λ its scaled counterpart. Using (3.25) we obtain

$$\begin{aligned} E_\mathrm{D}^\lambda = \sum_{i=1}^{N} A \int \psi_i^{\lambda *} \{(\varrho^\lambda)^{2/3} - (\varrho_{00}^\lambda)^{2/3} \\ - [(\varrho^\lambda)^{1/3} - (\varrho_0{}^\lambda)^{1/3}]^2\} \psi_i{}^\lambda \mathrm{d}v, \end{aligned} \tag{4.4}$$

where A is the constant in (3.25). Using (4.1) and (4.2) we obtain

$$\begin{aligned} E_\mathrm{D}^\lambda &= \lambda^2 \sum_{i=1}^{N} A \int \psi_i{}^*(\lambda\boldsymbol{r}) \{[\varrho(\lambda\boldsymbol{r})]^{2/3} \\ &\quad - [\varrho_{00}(\lambda\boldsymbol{r})]^{2/3} - ([\varrho(\lambda\boldsymbol{r})]^{1/3} \\ &\quad - [\varrho_0(\lambda\boldsymbol{r})]^{1/3})^2\} \psi_i(\lambda\boldsymbol{r}) \,\mathrm{d}(\lambda v) \\ &= \lambda^2 E_\mathrm{D}. \end{aligned} \tag{4.5}$$

Using this result we get for (2.23)

$$\begin{aligned} E_\mathrm{T}^\lambda &= E_k^\lambda + E_p^\lambda + E_\mathrm{D}^\lambda \\ &= \lambda^2(E_k + E_\mathrm{D}) + \lambda E_p. \end{aligned} \tag{4.6}$$

Since the pseudo-orbitals and the densities are defining the minimum of the total energy we must have

$$\lim_{\lambda=1} (\partial E_\mathrm{T}^\lambda / \partial\lambda) = 0, \tag{4.7}$$

from which we get

$$\begin{aligned} &\lim_{\lambda=1} [2\lambda(E_k + E_\mathrm{D}) + E_p] \\ &\qquad = 2(E_k + E_\mathrm{D}) + E_p = 0 \ , \end{aligned} \tag{4.8}$$

showing that the energy expression (2.23) satisfies the virial theorem with the potential (3.25).

Turning now to the potential (3.26) we note that, in accordance with their definitions, the radial densities are scaled as follows:

$$D_l{}^{\lambda} = \lambda D_l(\lambda r), \tag{4.9}$$

and

$$P^{\lambda}_{nl} = \lambda^{1/2} P_{nl}(\lambda r). \tag{4.10}$$

On putting these expressions into (3.26) and the resulting scaled potential into (4.3) we obtain

$$\begin{aligned} E^{\lambda}_{\mathrm{D}} = {} & \sum_{i=1}^{N} B \int \psi_i{}^{\lambda *} \\ & \cdot \{(D_l{}^{\lambda})^2 + 2(D_l{}^{\lambda})(P^{\lambda}_{nl})^2\} \psi_i{}^{\lambda} \, \mathrm{d}v \\ = {} & \lambda^2 \sum_{i=1}^{N} B \int \psi_i{}^{*}(\lambda \boldsymbol{r}) \{[D_l(\lambda r)]^2 \\ & + 2[D_l(\lambda r)][P_{nl}(\lambda r)]^2\} \\ & \cdot \psi_i(\lambda \boldsymbol{r}) \, \mathrm{d}(\lambda v) = \lambda^2 E_{\mathrm{D}} \end{aligned} \tag{4.11}$$

and putting this into (4.6) we arrive again at the result (4.8) showing that the potential (3.26) also satisfies the virial theorem.

This derivation demonstrates also that the virial theorem is satisfied regardless of the choice of the η parameter which is in the constants A and B. Since we know that the virial theorem is satisfied by $X\alpha$ regardless of the value of α we now can formulate the role of the two adjustable constants as follows. The strength of the exchange potential in (2.5) and the strength of the pseudopotentials (3.25) or (3.26) is regulated by the constants α and η respectively. Regardless of the choice of these parameters the virial theorem is satisfied. Specifically if the parameters are used to match the Hartree-Fock total energies then the potential and kinetic energies will separately match the corresponding HF values. It is also interesting to note that in this model the exchange energy is a potential energy while the pseudopotential energy is purely kinetic.

V. The Demonstration of the Shell-Structure of Atoms

What we usually mean in the Quantum Mechanics by the "shell-structure" of atoms is demonstrated in Fig. 2 where we have plotted the total radial density of the Kr atom obtained by HF-calculations [19] (full line) and by the all-electron single-Zeta calculations [3] (dashed line). The total radial density shows marked peaks corresponding to the K, L, M electron shells. In the Hartree-Fock model this structure appears after the calculations are carried out and the results plotted but they are not evident from the HF equations.

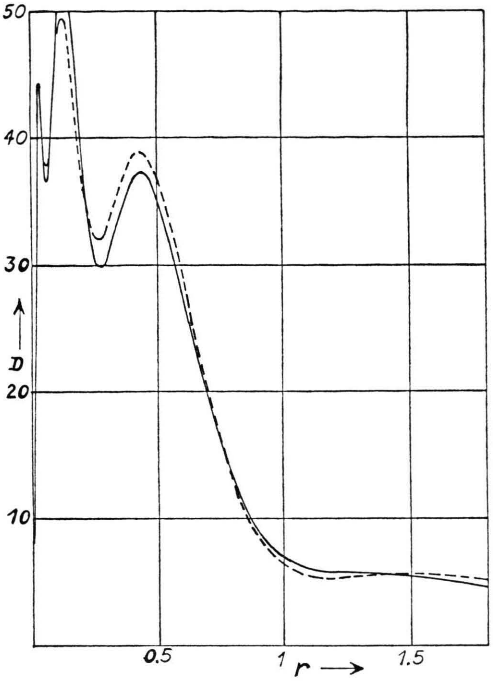

Fig. 2. The total radial electron density of the Kr atom. Full line: Hartree-Fock calculations; Dashed line: all-electron single Zeta calculations.

As the first application of our model we shall show now that it explains the shell structure without any calculations. This will be demonstrated by proving the following statement:

Effective potential theorem: "In the pseudopotential model an electron with quantum numbers (nl) moves in am effective potential which is (very nearly) independent of l, e.g. the effective potential depends, in a very good approximation, only on the principal quantum number n." [The phrase "in a very good approximation" will be clarified below.]

The shell structure follows from this theorem since if the theorem is true then the pseudo-orbitals for the (ns), (np), (nd) ... etc. electrons will be the solutions, in a very good approximation, of the same equation therefore their maxima will be (almost) at the same point giving rise to the shell structure as demonstrated by the typical density of Figure 2.

We prove the theorem by using (3.26) which has given excellent results in the all-electron single-Zeta calculations. We put $\psi_1 \ldots \psi_N$ in central field form

$$\psi_i \equiv \psi_{nlm} = \frac{P_{nl}}{r} Y_{lm}, \tag{5.1}$$

where P_{nl} is a nodeless pseudo-orbital and Y_{lm} is the normalized spherical harmonics. We obtain from (3.24) using (3.26), (2.4) and (2.5) the equation for the pseudo-orbital

$$\left(-\frac{1}{2}\frac{\mathrm{d}^2}{\mathrm{d}r^2} + V_{\text{eff}}\right) P_{nl} = \varepsilon_{nl} P_{nl}, \tag{5.2}$$

where the effective potential is given as

$$V_{\text{eff}} = -\frac{Z}{r} + \frac{l(l+1)}{2r^2} + V_{\text{c}}(r) - \frac{4}{3}\alpha\varrho^{1/3} + \eta\frac{\pi^2}{8(2l+1)^2}[D_l{}^2 + 2D_l P_{nl}^2]. \tag{5.3}$$

In this formula V_{c} is the electrostatic potential of all electrons including (nl):

$$V_{\text{c}}(r) = \int \frac{\varrho(r')\,\mathrm{d}v'}{|\boldsymbol{r} - \boldsymbol{r}'|}, \tag{5.4}$$

where ϱ is the spherically symmetric total density, and the radial density D_l appearing in the pseudopotential is given by (3.23):

$$D_l = \sum_{n'=1}^{n-1} q(n'l) P_{n'l}^2. \tag{5.5}$$

We have quoted above the equation connecting the radial and azimuthal momenta with the Fermi momentum, Equation (3.16). Using p_0 for p_{F} we obtain, taking into account (3.11), (3.17) and (3.18):

$$\tfrac{1}{2}(3\pi^2)^{2/3}\varrho_0{}^{2/3} = \frac{\pi^2 D_l{}^2}{8(2l+1)^2} + \frac{(l+\frac{1}{2})^2}{2r^2}. \tag{5.6}$$

Using this equation we get for the first term of the pseudopotential in Eq. (5.3):

$$\frac{\pi^2 D_l{}^2}{8(2l+1)^2} = \frac{1}{2}(3\pi^2)^{2/3}\varrho_0{}^{2/3} - \frac{(l+\frac{1}{2})^2}{2r^2}, \tag{5.7}$$

where we have put $\eta = 1$. Now putting this into (5.3) we obtain

$$V_{\text{eff}} = -\frac{Z}{r} + V_{\text{c}}(r) - \frac{4}{3}\alpha\varrho^{1/3} + \tfrac{1}{2}(3\pi^2)^{2/3}\varrho_0{}^{2/3} - \frac{1}{8r^2} + \frac{\pi^2 D_l P_{nl}^2}{4(2l+1)^2}. \tag{5.8}$$

It is easy to see that this effective potential is, apart from the last term, independent of l. The first three terms are the $X\alpha$ potential which depends only on the total density ϱ therefore is the same for all electrons. The next term with the $\varrho_0{}^{2/3}$, is the principal term of the pseudopotential, which was introduced through Equation (5.7). Now as we stated above there must be a one-to-one relationship between D_l and ϱ_0. As we see from (5.5) for an electron with principal quantum number n the radial density D_l is the radial density of all l-electrons in the lower lying shells i.e. in the shells with quantum numbers $1, 2, \ldots, (n-1)$. Correspondingly, ϱ_0 must be the total density of all electrons in those lower lying shells i.e. we must put

$$\varrho_0 = \sum_{n'=1}^{n-1}\sum_{l'=0}^{n'=1} q(n'l') P_{n'l'\,4\pi r^2}^2. \tag{5.9}$$

This expression depends clearly only on n (through the upper limit of the summation) therefore it is l-independent which means that the $\varrho_0{}^{2/3}$ term of the pseudopotential is l-independent. The term next to the last in (5.8) is an l-independent azimuthal energy which remains after the azimuthal term resulting from the Laplacian and the azimuthal term in (5.7) nearly cancel each other.

Now we can write

$$V_{\text{eff}} = V(n) + V'(n, l), \tag{5.10}$$

where $V(n)$ consists of the first five terms of (5.8) and V' is the last term

$$V'(n, l) = \frac{\pi^2 D_l P_{nl}^2}{4(2l+1)^2}. \tag{5.11}$$

It is evident that V' is small relative to the $\varrho_0{}^{2/3}$ term which corresponds to the $D_l{}^2$ term in (5.3). In V' D_l is the radial density of all electrons with the principal quantum number $1, 2, \ldots, (n-1)$ and the azimuthal quantum number l; P_{nl}^2 is the radial density of the selected electron. V' will be different from zero only in those regions where there is an overlap between D_l and P_{nl}^2. Since these quantities refer to electrons with different n, the overlap area will not be too large. The pseudopotential term containing $D_l{}^2$ in (5.3) will certainly be much larger. It is clear that V' will be small but it is also clear from this argument that it will not be negligible.

Summarizing our results, Eq. (5.10) shows that the effective potential consists of two terms, the first of which, $V(n)$ is independent of l; the second term V' depends on l but is small relative to $V(n)$. The "effective potential theorem" is thereby proved.

We see now that the effective potentials for the $(n\mathrm{s})$, $(n\mathrm{p})$, $(n\mathrm{d})$, etc. electrons differ only in the V' term. A typical result is the set of Zeta parameters which we obtained for the Kr atom from the APM single Zeta calculations [3] (these parameters were used to plot the density curve in Figure 2). These are as follows:

$$\begin{array}{lll} \zeta(1\mathrm{s}) = 37.52; & \zeta(3\mathrm{s}) = 5.27; & \zeta(4\mathrm{s}) = 2.20; \\ \zeta(2\mathrm{s}) = 12.02; & \zeta(3\mathrm{p}) = 6.60; & \zeta(4\mathrm{p}) = 2.70; \\ \zeta(2\mathrm{p}) = 16.80; & \zeta(3\mathrm{d}) = 7.00. & \end{array} \tag{5.12}$$

The Zeta's with the same n (electrons in the same shell) are grouped close together and the difference between the Zeta's belonging to the same n but different l is small but not negligible in accordance with our analysis of the V'. The Zeta parameters show similar characteristics for all atoms for which we made calculations [3]. The pseudopotential model explains the shell structure of atoms and it explains not only the salient features but the fine details as well.

[1] J. C. Slater, Adv. Quant. Chem. **6**, 1 (1972). This is a review article containing extensive and accurate references to earlier work.

[2] L. Szasz, J. Chem. Phys. **64**, 492 (1976); Z. Naturforsch. **33a**, 1210 (1978).

[3] L. Szasz, J. Chem. Phys. in print.

[4] H. Hellmann, J. Chem. Phys. **3**, 61 (1935).

[5] P. Gombas, Z. Physik **118**, 164 (1941).

[6] P. Szepfalussy, Acta Phys. Hung. **5**, 325 (1955); **6**, 273 (1956).

[7] J. C. Phillips and L. Kleinmann, Phys. Rev. **116**, 287 (1959); **118**, 1153 (1960).

[8] M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

[9] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

[10] L. Szasz, J. Chem. Phys. **49**, 679 (1968).

[11] J. D. Weeks and S. Rice, J. Chem. Phys. **49**, 2741 (1968).

[12] W. H. E. Schwarz, Theor. Chim. Acta Berlin **11**, 307 (1968).

[13] L. Szasz, Z. Naturforsch. **32a**, 252 (1977); **32a**, 829 (1977).

[14] E. Fermi, Z. Physik, **48**, 73 (1928).

[15] P. Gombas, Acta Phys. Hung. **1**, 285 (1952).

[16] A review of the density-dependent pseudopotentials and their applications is given in the book of P. Gombas, Pseudopotentiale, Springer-Verlag, Wien 1967.

[17] W. H. E. Schwarz, Acta Phys. Hung. **27**, 391 (1969).

[18] V. Fock, Phys. Z. USSR **1**, 747 (1932).

[19] C. Froese-Fischer, Atomic Data **4**, 301 (1972).