

## Symmetry Effects on SINGLET & TRIPLET States in He.

ip (11)

As in Eq. (20), the overall wavefn will be  $\Psi(r_k, \sigma_k) = u(r_k) \chi(\sigma_k)$ ,  $k=1, 2$ , and this  $\Psi$  must have odd exchange symmetry, because we are dealing with two fermions. Even though the dipole-dipole interaction is not explicit in  $\mathcal{H}(1, 2)$  of Eq. (27), its existence will force the spin eigenstates  $\chi(\sigma_k)$  to be either the TRIPLET or SINGLET variety in Eq. (16). Then, since the  $\chi(\sigma_k)$  show exchange symmetry [(+) for TRIPLET, (-) for SINGLET], the space eigenstates  $u(r_k)$  must also show exchange symmetry [(-) for TRIPLET, (+) for SINGLET]. That is:

$$\left\{ \begin{array}{l} \text{for } \chi = \text{spin } \underline{\text{TRIPLET}} \text{ eigenstate : } u(r_1, r_2) = u^-(r_1, r_2), \text{ odd space state;} \\ \text{for } \chi = \text{spin } \underline{\text{SINGLET}} \text{ eigenstate : } u(r_1, r_2) = u^+(r_1, r_2), \text{ even space state.} \end{array} \right. \quad (28)$$

Assume the electrons are in different individual states  $\phi_\alpha \neq \phi_\beta$ , and use the overall symmetrized states  $u^\pm(r_1, r_2)$  of Eq. (21) to calculate the system energies:

$$\begin{aligned} \rightarrow E_{S,T} &= \langle u^\pm(r_1, r_2) | \mathcal{H}(1, 2) | u^\pm(r_1, r_2) \rangle \quad \begin{array}{l} \text{upper sign, } u^+ \Rightarrow \underline{\text{SINGLET}} \text{ state } S, \\ \text{lower sign, } u^- \Rightarrow \underline{\text{TRIPLET}} \text{ state } T; \end{array} \\ &= (E_\alpha + E_\beta) + \frac{1}{2} \langle \phi_\alpha(1) \phi_\beta(2) \pm \phi_\beta(1) \phi_\alpha(2) | \frac{e^2}{r_{12}} | \phi_\alpha(1) \phi_\beta(2) \pm \phi_\beta(1) \phi_\alpha(2) \rangle \quad (29) \end{aligned}$$

... expand, and use  $r_{21} = r_{12}$ , to get...

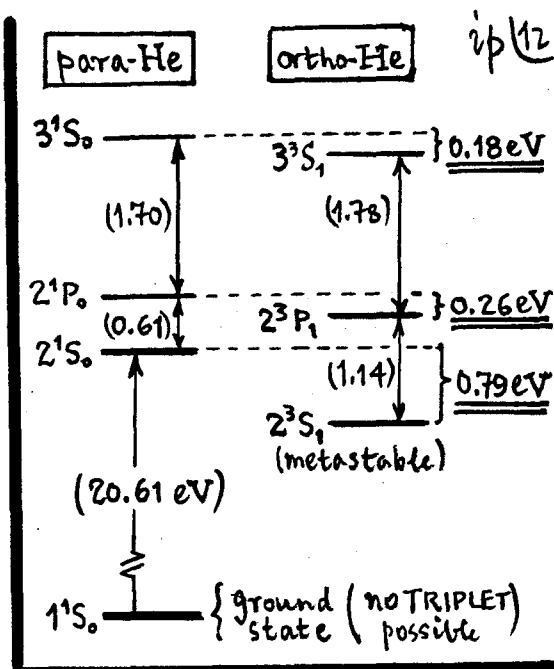
$$\left\{ \begin{array}{l} \boxed{E_{S,T} = (E_\alpha + E_\beta) + J \pm K} \leftarrow \text{SINGLET, TRIPLET energies;} \\ \text{w// } J = \langle \phi_\alpha(1) \phi_\beta(2) | \frac{e^2}{r_{12}} | \phi_\alpha(1) \phi_\beta(2) \rangle \quad \begin{array}{l} \text{called:} \\ \text{Coulomb "direct integral";} \end{array} \\ K = \langle \phi_\alpha(1) \phi_\beta(2) | \frac{e^2}{r_{12}} | \phi_\beta(1) \phi_\alpha(2) \rangle \quad \begin{array}{l} \text{called:} \\ \text{Coulomb "exchange integral";} \end{array} \end{array} \right. \quad (30)$$

So here we see a direct effect on the system energies due to exchange symmetry. Had we used the non-symmetrized space state  $u(r_1, r_2) = \phi_\alpha(1) \phi_\beta(2)$ , the term in  $J$  would still have been present, but not  $K$ ...  $K$  appears as a result of symmetrizing  $u$  to  $u^\pm$ . With  $K > 0$ , the measurable physical effect is:

$$\rightarrow E_S - E_T = 2K \Rightarrow \underline{\text{SINGLET states are less tightly bound than TRIPLET states.}} \quad (31)$$

## Actual SINGLET-TRIPLET corrections to He-spectrum.

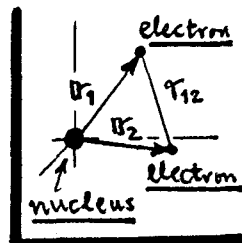
9) That TRIPLET states lie lower than SINGLETs in He is confirmed by experiment. A level diagram of low-lying states in He is shown at right. The numbers at the far right show the depression of the TRIPLET state relative to its companion SINGLET in the same shell -- e.g. in shell #2, the  $^3S_1$  state lies lower than  $^1S_0$  by 0.79 eV; the effect of exchange here is  $\sim 4\%$  of the binding for 2S, so the exchange corrections contribute non-trivially to the He spectrum.



## REMARKS

1. The TRIPLET [T] - SINGLET [S] defect can be thought of in terms of the previously calculated electron separation. By Eq. (28), the T-state space wavefn is odd,  $u^-$ , and by (25) the inter-electron spacing  $r_{12}$  is larger than usual because of exchange symmetry; this reduces the electron repulsion energy  $\frac{e^2}{r_{12}}$ . By comparison, the S-state wavefn is even,  $u^+$ , so the spacing  $r_{12}$  is smaller than usual; this increases the e-e repulsion  $\frac{e^2}{r_{12}}$ . So the SINGLET states are less tightly bound because the e's are forced closer together by exchange forces.

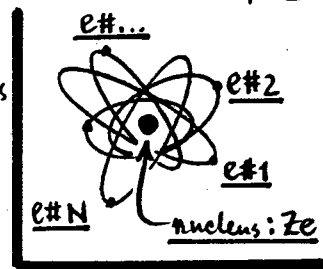
2. The Coulomb integrals  $J$  &  $K$  in Eq. (30) are  $\sim$  complicated [they are called "two-center integrals" because there are two integrations needed, one over  $\mathbf{r}_1$  and one over  $\mathbf{r}_2$ ], but they can be estimated to  $\sim 20\%$  accuracy by just putting the individual states  $\phi_\alpha$  &  $\phi_\beta$  = hydrogen atom wavefns, with  $Z=2$ . \* E.g. if  $\phi_\alpha$  = H-atom ground state (1s), and  $\phi_\beta$  = H-atom first excited state (2p), one calculates the  $2^1P_0 - 2^3P_1$  splitting in He to be  $\Delta E(2P) = 2K(1s, 2p) = 0.21 \text{ eV}$ . This compares with the observed 0.26 eV.



## The problem of the N-electron atom.

ip(13)

2) A problem of abiding interest in the QM of identical particles has been that of calculating the energy levels of an N-electron atom,  $\forall N \geq 2$ . In lowest order, the system  $\text{Ham}^n$  is:



$$\rightarrow \mathcal{H}(1,2,\dots,N) = \sum_{k=1}^N \left[ -(\hbar^2/2m) \nabla_k^2 - Ze^2/r_k \right] + \sum_{k>j}^N \sum_{j=1}^N (e^2/r_{jk}). \quad (31)$$

This  $\mathcal{H}$  ignores magnetic dipole-dipole interactions. Here  $m$  = electron mass,  $r_k$  is the position of the  $k^{\text{th}}$  electron w.r.t. an  $\infty$  ly heavy nucleus of charge  $Ze$ ,  $\nabla_k = \partial/\partial r_k$  is the gradient operator, and  $r_{jk} = |r_j - r_k|$  is the separation between  $j^{\text{th}}$  &  $k^{\text{th}}$  electron.

The Schrodinger problem is:  $\mathcal{H}\Psi = E\Psi$ ,  $\forall \Psi = \Psi(1,2,\dots,N)$  dependent on all  $N$  e's. Simplest question is: what eigenenergies  $E$  are allowed? The question of "what  $E$ 's?" has been answered  $\sim$  successfully by various approximation methods and brute-force computations, but even today -- after 60 years of effort -- reliable solutions for the wavefns  $\Psi$  are problematic. Consequently, calculations which depend on matrix elements of various operator w.r.t. to the  $\Psi$ 's (such as ionization processes, cross-sections for scattering of atoms with  $N_1$  &  $N_2$  electrons resp.) are not well-posed. In general, the  $N$ -body problem remains an active research field -- witness solid-state physics. In what follows, we will outline briefly some attacks on the question of "what  $E$ 's?" for  $\mathcal{H}$  of (31). We won't say much on "what  $\Psi$ 's?"

The e-e repulsion terms ( $e^2/r_{jk}$ ) in Eq. (31) prevent a strict separation-of-variables (for  $\mathcal{H}\Psi = E\Psi$ ) into  $N$  one-electron problems -- a procedure which would be possible if such terms were absent. However, the most successful (tractable) approximations are based on representing the potential energy terms in  $\mathcal{H}$  of (31) by a sum of one-electron potentials  $U(r_k)$ , so that  $\mathcal{H}$  of Eq. (31) is written:

$$\rightarrow \mathcal{H}(1,2,\dots,N) = \sum_{k=1}^N H_k, \quad \forall H_k = -(\hbar^2/2m) \nabla_k^2 + U(r_k). \quad (32)$$

## Separation into N one-electron problems, Slater Determinants.

ip(14)

When "suitable"  $U(r_k)$ 's can be found, then we can form product states of one-electron eigenfns  $\phi_\alpha(r)$ , i.e.

$$\rightarrow \Psi(1, 2, \dots, N) = \phi_\alpha(r_1) \phi_\beta(r_2) \dots \phi_\mu(r_N), \quad (33)$$

and find that  $\mathcal{H}\Psi = E\Psi$  generates N one-electron problems, viz

$$\rightarrow \mathcal{H}\Psi = E\Psi \Rightarrow \underline{H_k \phi_\lambda(r_k) = E_\lambda \phi_\lambda(r_k)} \quad \sqrt{\sum_{k=1}^N} \quad k=1 \text{ to } N; \lambda=\alpha, \beta, \dots, \mu; \quad \text{and total energy; } E = \sum_{\lambda} E_{\lambda}. \quad (34)$$

Producing "suitable"  $U(r_k)$ 's for:  $\underline{H_k = -\frac{\hbar^2}{2m} \nabla_k^2 + U(r_k)}$ , involves the most effort.

The product wavefn  $\Psi$  in Eq. (33) does not properly account for the electron exchange symmetry, which requires the overall wavefn  $\Psi(1, 2, \dots, N)$  be odd under exchange of any two electrons. Also  $\Psi$  in Eq. (33) does not include spin ... even though  $\mathcal{H}$  of Eq. (31) ignores dipole-dipole coupling, a spin labelling is ultimately essential to specify the state. What can be done is as follows:

$$\text{choose one-electron eigenfns} \left\{ \underline{\phi_\lambda(k) = \phi_\lambda(r_k) \chi(\sigma_k)} \right. \quad \sqrt{\begin{aligned} \phi_\lambda(r_k) &= \text{space state, per Eq. (34);} \\ \chi(\sigma_k) &= |S_k, m_k\rangle = \text{spin state} \end{aligned}} \quad (35)$$

$\left\{ \begin{aligned} S_k &= 1/2 \\ m_k &= \pm 1/2 \end{aligned} \right.$

... Construct the "Slater-Determinant Wavefn"...

$$\rightarrow \Psi(1, 2, \dots, N) = \frac{1}{\sqrt{N!}} \det \begin{bmatrix} \phi_\alpha(1) & \phi_\alpha(2) & \dots & \phi_\alpha(N) \\ \phi_\beta(1) & \phi_\beta(2) & \dots & \phi_\beta(N) \\ \vdots & \vdots & & \vdots \\ \phi_\mu(1) & \phi_\mu(2) & \dots & \phi_\mu(N) \end{bmatrix}. \quad (36)$$

The det has  $N!$  terms, each an  $N$ -fold product of the  $\phi_\lambda(k)$ , with all possible perm<sup>n</sup>s of  $\lambda \neq k$ .

By the rules of determinants, if any two particles are exchanged (say  $1 \leftrightarrow 2$ )  $\Psi$  changes sign as required (because, for the determinant, this is equivalent to interchanging two columns  $\Rightarrow$  det changes sign). Also, the Slater  $\Psi$  respects the Pauli Exclusion Principle: no two electrons can be in the same state... if (say)  $\beta \equiv \alpha$ , then two rows of the det are identical, and the det  $\equiv 0 \neq \Psi \equiv 0$ . But we won't use Slater's  $\Psi$  initially. We focus first on the  $U(r_k)$ 's in Eq. (34).

## Asymptotic forms for the one-electron potential $U(r_k)$ .

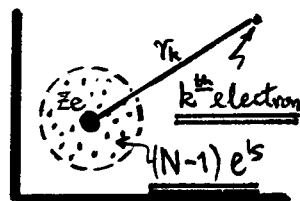
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- 10) It would be "nice" if in  $\mathcal{H}$  of Eq. (31) we could neglect the e-e repulsion terms  $(e^2/r_{jk})$  to zero<sup>th</sup> order and then treat them by perturbation theory. But this won't work here, because although any one of the  $(e^2/r_{jk})$  may be small compared to the nuclear binding  $(Ze^2/r_k)$ , there are so many of them [namely:  $\frac{1}{2}N(N-1)$ ] that their total effect is comparable to the binding. So the terms  $(e^2/r_{jk})$  must be dealt with in some other way. That is what motivates trying to write  $\sum_{k=1}^N \left[ -\frac{Ze^2}{r_k} + \sum_{j \neq k} \frac{e^2}{r_{jk}} \right]$  as a sum of one-electron potentials  $U(r_k)$ .

To get an idea of what a "reasonable"  $U(r_k)$  might be, we consider the limits  $r_k \rightarrow \infty$  and  $r_k \rightarrow 0$ . For  $r_k$  "large" compared to the other  $r_{j \neq k}$ , have  $r_{jk} \approx r_k$ , and  $(e^2/r_{jk}) \approx e^2/r_k$ . Since there are  $(N-1)$  values of  $j$  for each  $k$ , then the e-e repulsion for the  $k^{\text{th}}$  electron is  $\approx (N-1)e^2/r_k$ , and it moves in

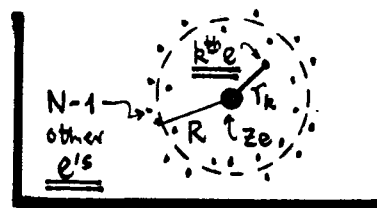
$$\underline{U(r_k) \approx -[Z - (N-1)]e^2/r_k}, \text{ as } r_k \rightarrow \infty. \quad (37)$$

As  $r_k \rightarrow \infty$  (the  $k^{\text{th}}$  e is far away from the nucleus), the  $(N-1)e^s$  left behind screen the nuclear charge from  $Z$  to  $[Z - (N-1)]$ .



But now when  $r_k$  approaches the value of the other  $r_{j \neq k}$ , the screening becomes poorly defined -- only when  $r_k$  is "small" compared to the  $r_{j \neq k}$  can we again say something about how  $U(r_k)$  behaves. As  $r_k \rightarrow 0$ , the  $k^{\text{th}}$  electron "sees" the fully unscreened nucleus, and also interacts with the outlying  $e^s$  -- whose effect we can account for approximately by assuming that the  $(N-1)$  outlying  $e^s$  are distributed  $\sim$  spherically symmetrically at mean distance  $R$  from the nucleus. In this case, we can write...

$$\underline{U(r_k) \approx -Ze^2/r_k + (N-1)e^2/R}, \text{ as } r_k \rightarrow 0. \quad (38)$$



The asymptotic forms in (37) & (38) must characterize any one-electron potential  $U(r_k)$ . Now, specialize to  $N=Z$  (<sup>neutral</sup> atom) and try to find "reasonable" forms for  $U(r_k)$ .

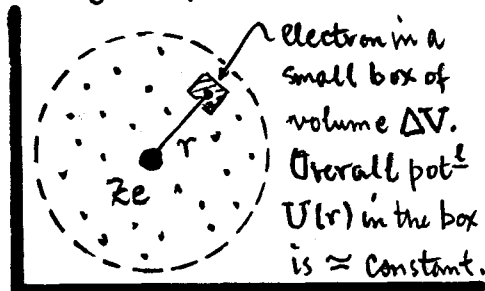
## Thomas-Fermi model for $U(r)$ : the statistical atom.

THOMAS-  
FERMI 1

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- 1) A first attempt to derive a reasonable  $U(r_k)$  depended on a statistical (sic!) model of a many-electron atom. The model was developed independently by Thomas and Fermi,<sup>†</sup> and it works best for atoms with a large #  $N$  of electrons.

1. We begin a description of the Thomas-Fermi model by imagining the space surrounding the nucleus to be divided up into a large # of small "boxes", such that the overall potential  $U(r)$  of a single electron within a given box is  $\approx$  constant. We assume spherical symmetry, so that  $U$  is a fn of  $r$ , rather than  $\mathbf{r}$ . The energy states available to the electron-in-a-box should range from  $U(r)$  [for zero kinetic energy] up to 0 [for max. K.E. =  $-U(r)$ , with  $U(r)$  negative for binding]. Then the electron-in-a-box can have its momentum distributed from  $p=0$  up to  $p_{\max} = [-2mU(r)]^{1/2}$ .



2. If  $k = p/\hbar$  is the wave# of our electron-in-a-box (where  $U(r) \approx \text{const}$ ), then the # of distinct energy states per unit volume available between  $k$  &  $k+dk$  is just  $dn/\Delta V = 2 \cdot 4\pi k^2 dk / (2\pi)^3$ .<sup>\*</sup> Since these states are occupied from  $k=0$  up to  $k_{\max} =$

<sup>\*</sup> Let the box be rectangular, with sides of length  $l \ll r$ . For  $U(r) \approx \text{const}$  in the box, and for periodic boundary conditions, the wave vector  $\mathbf{k}$  of the electron will have its components  $k_i$  ( $i=x,y,z$ ) quantized per:  $k_i l = 2\pi n_i$ ,  $\forall n_i = 1, 2, 3, \dots$ . Then  $dn_i = dk_i / (2\pi/l)$ , and the # distinct  $\mathbf{k}$ -states possible in the volume  $d^3k$  at  $\mathbf{k}$  is:  $dn = \left(\frac{dk_x}{2\pi/l}\right) \left(\frac{dk_y}{2\pi/l}\right) \left(\frac{dk_z}{2\pi/l}\right) = [\Delta V / (2\pi)^3] d^3k$ ,  $\forall \Delta V = l^3$ . So:  $dn/\Delta V = d^3k / (2\pi)^3$ , is the # states/unit volume. If the direction of  $\mathbf{k}$  is not relevant, then  $\mathbf{k}$  is spherically symmetric, and  $d^3k \rightarrow 4\pi k^2 dk$  (non-directional spherical shell in  $\mathbf{k}$ -space). Finally, when there are two spin states for each  $\mathbf{k}$ , we multiply by 2 to obtain:  $dn/\Delta V = 2 \cdot 4\pi k^2 dk / (2\pi)^3$ , as used above.

<sup>†</sup> L.H. Thomas, Proc. Camb. Phil. Soc. 23, 542 (1927); E. Fermi, Z. Physik 48, 73 (1928). Most recently, J.S. Schwinger has worked on this problem.

## Derivation of Thomas-Fermi Eq. for Screening Fcn. $\phi$ .

THOMAS-  
FERMI 2

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$= p_{\max}/\hbar = [-(2m/\hbar^2)U(r)]^{1/2}$ , then the total # distinct electron states available in the "box" of physical volume  $\Delta V$  is ...

$$\rightarrow \Delta n = \Delta V \int_0^{k_{\max}} 2 \cdot 4\pi k^2 dk / (2\pi)^3 = \Delta V \cdot k_{\max}^3 / 3\pi^2, \quad k_{\max} = \left[ -\frac{2m}{\hbar^2} U(r) \right]^{1/2}$$
$$\Rightarrow \text{density of states} \} \quad \underline{\rho(r) = \Delta n / \Delta V = [-2m U(r)]^{3/2} / 3\pi^2 \hbar^3.} \quad (39)$$

If  $\Delta n$  distinct states are available in  $\Delta V$ , then there can be  $\Delta n$  electrons in that volume at max. (this respects the Exclusion Principle), so at full occupation, the box will show an electron charge density:  $(-e)\rho(r)$ .

3. When the atom settles into a minimum energy state, the boxes  $\Delta V$  will be fully occupied -- starting with those in close to the nucleus, and extending out to a value of  $r$  sufficient to accommodate all  $N$  electrons (actually  $r \rightarrow \infty$ ). Then the charge density  $(-e)\rho(r)$  of Eq. (39) determines an effective potential  $U(r)$  which -- classically -- can be found from Poisson's Equation:

$$\rightarrow \nabla^2 \left[ -\frac{1}{e} U(r) \right] = -4\pi [(-e)\rho(r)]. \quad (40)$$

Plug in  $\rho(r)$  of Eq. (39), and use  $\nabla^2 = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d}{dr} \right)$  for radial fcn  $r$ ...

$$\rightarrow \frac{1}{r^2} \frac{d}{dr} \left[ r^2 \frac{d}{dr} (-U) \right] = \frac{4e^2 (2m)^{3/2}}{3\pi \hbar^3} [-U]^{3/2}. \quad (41)$$

Now make the following substitutions...

$$\left[ \begin{array}{l} U(r) = -\frac{Ze^2}{r} \phi(x), \quad x = \frac{r}{b} \leftarrow \phi(x) \text{ is the Thomas-Fermi screening fcn;} \\ b = \frac{1}{2} \left( \frac{3\pi}{4} \right)^{2/3} \frac{\hbar^2}{me^2 Z^{1/3}} = 0.8853 a_0 / Z^{1/3}, \quad a_0 = \frac{\hbar^2}{me^2} = 0.529 \times 10^{-8} \text{ cm} \sqrt{\text{BOHR RADIUS}} \end{array} \right]$$

Sq. Eq. (41) becomes:  $\boxed{x^{1/2} (d^2 \phi / dx^2) = \phi^{3/2}}. \quad (42)$

This is the Thomas-Fermi equation for the screening fcn  $\phi$ . It is a 2nd order nonlinear differential eqn; a solution is not possible in terms of elementary fcn. A numerical solution is needed. NOTE:  $\phi$  is a universal fcn of  $x$ , % parameters.

## Solution for the Thomas-Fermi screening for $\phi(x)$ .

THOMAS-  
FERMI 3

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4. It is important to notice that the Thomas-Fermi Eqn, Eq. (42), does not contain the atomic #  $Z$  explicitly, so its solution  $\phi(x)$  defines a universal fn of  $x$  -- good for all atoms  $Z$ . Of course  $Z$  is still in the problem, through the scale length  $b = 0.8853 a_0 / Z^{1/3}$  used in defining  $x = r/b$ .

The Thomas-Fermi Eqn is solved with the following boundary conditions:

- ①  $\lim_{r \rightarrow \infty} [r U(r)] = 0$   $\checkmark$  there is no net charge within a very large sphere surrounding the neutral atom;  $\Rightarrow \phi(x \rightarrow \infty) = 0$ ;
- ②  $\lim_{r \rightarrow 0} [U(r)] = (-) \frac{Ze^2}{r}$   $\checkmark$  the potential near the nucleus must be that of the unshielded nucleus;  $\Rightarrow \phi(x \rightarrow 0) = 1$ . (43)

B.C. #1 here is a bit stronger than that of Eq. (37). B.C. #2 conforms to Eq. (38) with the const term  $(N-1)e^2/R$  being dropped.

The result of a numerical solution to the Thomas-Fermi Eqn, Eq. (42), is shown at right. The screening fn  $\phi(x)$  falls off more slowly than a Yukawa-type screening factor  $e^{-x}$ , but certainly decreases rapidly --  $\phi(x)$  is down by a factor  $\sim 10$  at  $x=4$ . A reasonable analytic fit to the calculated curve is:

$$\phi(x) = 1 / \left[ 1 + \sum_{n=1}^6 C_n x^{n/2} \right], \quad (44)$$

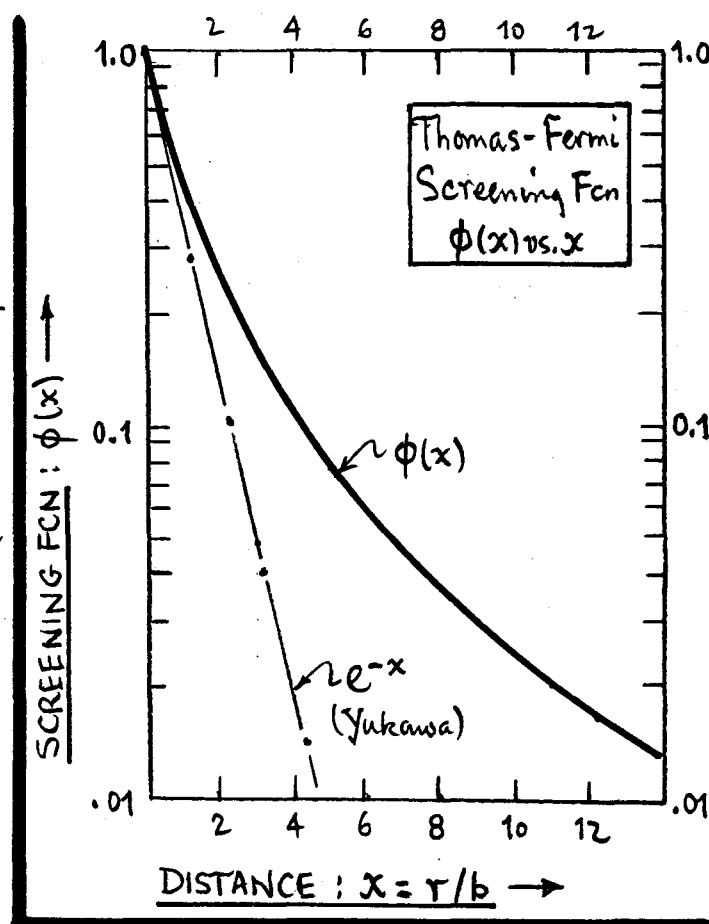
$$C_1 = 0.02747, C_2 = 1.243, C_3 = -0.1486,$$

$$C_4 = 0.2403, C_5 = 7.30 \times 10^{-3}, C_6 = 6.94 \times 10^{-3}.$$

With this, the Thomas-Fermi effective

potential for a neutral atom of atomic #  $Z$  is:  $\underline{U(r) = (-) \frac{Ze^2}{r} \phi(x)}$ ,  $x = \frac{r}{b}$

and  $b = 0.8853 a_0 / Z^{1/3}$ .





5. The next step, after obtaining a numerical representation of  $\phi(x)$  such as in Eq. (44), is to use  $U(r) = -\frac{Ze^2}{r} \phi(x)$  in the  $N$  one-electron problems of Eq. (34), viz:  $[-(\hbar^2/2m)\nabla^2 + U(r)]\phi_\lambda(r) = E_\lambda \phi_\lambda(r)$ . This is a central-force problem, but with a ~spectacularly complicated potential  $U(r)$ . More numerical work is needed.

The first comprehensive numerical work for solving the one-electron problem for a Thomas-Fermi potential  $U(r)$  was done by R. Latter, Phys. Rev. 99, 510 (1955). Some of his results are shown below [his Figs. 8 & 9, for  $\sqrt{(\text{binding energy})}$  vs.  $Z$ , for one-electron s & p states]. The results agree with experimental values fairly well (esp. on a log-log plot), particularly for high  $Z$  atoms, where the statistical model works best. Shown on the graphs are the Thomas-Fermi energies (solid lines) and also Thomas-Fermi-Dirac energies (dashed lines)... the latter correct the "pure" Thomas-Fermi theory for electron correlations (i.e. exchange symmetry). Clearly,

exchange corrections are "small" as  $Z \rightarrow \text{large}$ . Also shown; some values calculated via Hartree and Hartree-Fock theory. We examine that theory next.

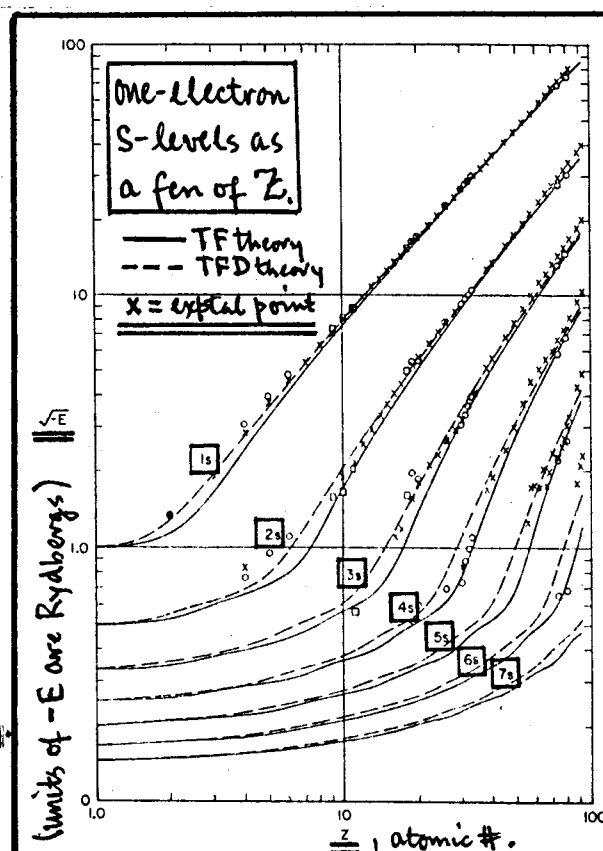


FIG. 9. The square root of the computed s-levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (O) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (X) are the experimental values.

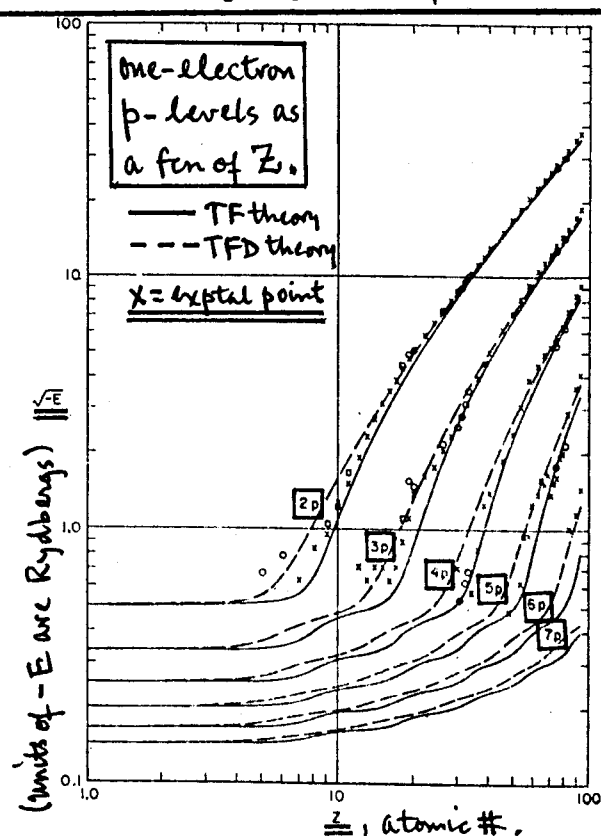


FIG. 10. The square root of the computed p-levels are shown with the solid line for the Thomas-Fermi atom and with the dashed line for the Thomas-Fermi-Dirac atom. The circles (O) are the values computed by the Hartree method; the squares (□) are the values computed by the Hartree-Fock method. The crosses (X) are the experimental values where the doublet energies have been averaged.