

## INTRODUCTION

Atoms that contain many electrons possess a degree of complexity so high that it is impossible to give an exact answer even when we are asking simple questions. We are therefore compelled to resort to approximate descriptions. Two main approaches have been pursued in theoretical atomic physics. One is the Hartree-Fock (HF) method and its refinements; it can be viewed as a generalization of Schrödinger's description of the hydrogen atom to many-electron systems; it is, by construction, the more reliable the smaller the number of electrons. The other one is the Thomas-Fermi (TF) treatment and its improvements; this one uses the picture of an electronic atmosphere surrounding the nucleus; it is the better the larger the number of electrons. For this reason, the TF method is frequently called the "statistical theory of the atoms."

Throughout these lectures we shall be concerned with the TF approach, thereby concentrating on more recent developments. The repetition of material that has been presented in textbooks<sup>1</sup> already will be limited to the minimal amount necessary to make the lectures self-contained. The derivation of known results will, wherever feasible, be done differently, and - I believe - more elegantly, than in standard texts on the subject.

It should be realized that the methods of the TF approach are in no way limited to atomic physics. Besides the immediate modifications for applying the formalism to molecules or solids, there exists the possibility of employing the technics in astrophysics and in nuclear physics. The latter application naturally requires appropriate changes reflecting the transition from the Coulomb interaction of the electrons to the much more complicated nucleon-nucleon forces.

In these lectures we shall confine the discussion to atoms, however. This has the advantage of keeping the complexity of most calculations at a rather low level, so that we can fully focus on the properties of the TF method without being distracted by the technical complications that arise from the considerations of molecular structure or from our incomplete knowledge of the nuclear forces, for instance. Restricting ourselves to atoms is further advantageous because it enables us to compare predictions of TF theory with those of other methods, like HF calculations. The ultimate test of a theoretical description is,

of course, the comparison of its implications with experimental data. Whenever possible, we shall therefore measure the accuracy of the TF predictions by confronting it with experimental results.

Lack of experimental data sometimes forces us into relying upon HF results for comparison. The same situation occurs when quantities of a more theoretical nature are discussed (as, e.g., the nonrelativistic binding energy, which is not available from experiments). Such a procedure must not be misunderstood as an attempt of reproducing HF predictions by TF theory. The TF method is not an approximation to the HF description, but an independent approach to theoretical atomic physics. [Incidentally, it is the historically older one: TF theory originated in the years 1926 (Thomas) and 1927 (Fermi), whereas the HF model did not exist prior to 1928 (Hartree) and 1930 (Fock).]<sup>2</sup> The two approaches should not be regarded as competing with each other, but as supplementing one another. Each of the two methods is well suited for studying certain properties of atoms. For example, if one is interested in the ionization energy of oxygen, a HF calculation will produce a reliable result; but if you want to know how the total binding energy varies over the entire Periodic Table, the TF model will tell you. Tersely: the HF method for specific information about a particular atom, the TF method for the systematics of all atoms. There is, of course, a certain overlap of the two approaches, and they are not completely unrelated. We shall discuss their connection to some extent in Chapter Two.

Atomic units. All future algebraic manipulations are eased significantly when atomic units are used for measuring distances, energies, etc. Let us briefly consider the many-particle Hamilton operator

$$H_{mp} = \sum_{j=1}^N \frac{1}{2m} \vec{p}_j^2 - \sum_{j=1}^N \frac{Ze^2}{r_j} + \frac{1}{2} \sum_{j,k=1}^N{}' \frac{e^2}{r_{jk}} \quad (1-1)$$

of an atom with nuclear charge  $Ze$  and  $N$  electrons, each of mass  $m$  and carrying charge  $-e$ . The third sum is primed to denote the omission of the term with  $j = k$ . Obviously,  $r_j$  stands for the distance between the nucleus and the  $j$ -th electron, whereas  $r_{jk}$  is the distance from the  $j$ -th to the  $k$ -th electron, and  $\vec{p}_j$  the momentum of the  $j$ -th electron. This  $H_{mp}$  is accompanied by the commutation relations

$$[\vec{r}_j, \vec{p}_k] = i \hbar \vec{e} \delta_{jk} \quad (1-2)$$

and the injunctions caused by the Fermi statistics that the electrons obey. Equations (1) and (2) contain three dimensional parameters:  $m$ ,  $e$ ,  $\hbar$ . But none of them can possibly be used as expansion variable of a perturbation series because together they do no more than set the atomic scale. To see this in detail, let us rewrite (1) and (2) with the aid of the Bohr radius

$$a_0 = \frac{\hbar^2}{me^2} = 0.5292 \text{ \AA} \quad (1-3)$$

and twice the Rydberg energy

$$E_0 = \frac{e^2}{a_0} = \frac{me^4}{\hbar^2} = 27.21 \text{ eV}. \quad (1-4)$$

Equations (1) and (2) now appear as

$$H_{\text{mp}}/E_0 = \sum_j \frac{1}{2} (p_j/\frac{\hbar}{a_0})^2 - \sum_j \frac{Z}{(r_j/a_0)} + \frac{1}{2} \sum_{j,k}' \frac{1}{(r_{jk}/a_0)} \quad (1-5)$$

and

$$[(\vec{r}_j/a_0), (\vec{p}_k/\frac{\hbar}{a_0})] = i \overleftrightarrow{1} \delta_{jk} . \quad (1-6)$$

If we then introduce the dimensionless quantities  $\vec{r}_j/a_0$ ,  $\vec{p}_j/\frac{\hbar}{a_0}$ , and  $H_{\text{mp}}/E_0$  as relevant objects, all reference to  $m$ ,  $e$ , and  $\hbar$  disappears. Using the same letters as for the dimensional quantities, we now have

$$H_{\text{mp}} = \sum_j \frac{1}{2} p_j^2 - \sum_j \frac{Z}{r_j} + \frac{1}{2} \sum_{j,k}' \frac{1}{r_{jk}} \quad (1-7)$$

and

$$[\vec{r}_j, \vec{p}_k] = i \overleftrightarrow{1} \delta_{jk} . \quad (1-8)$$

Equations (7) and (8) are identical with Eqs. (1) and (2) except that instead of the macroscopic units (cm, erg, etc.) atomic units are used. Formally, the transition from (1) and (2) to (7) and (8) can be done by "setting  $e = \hbar = m = 1$ ," but the meaning of this colloquial procedure is made precise by the argument presented above.

Besides simplifying the algebra, the use of atomic units also prevents us from trying such foolish things like "expanding the energy in powers of  $\hbar$ ," a phrase that one meets surprisingly frequently in the literature. The energy is nothing but  $E_0$  times a dimensionless function of  $Z$  and  $N$ , it depends on  $\hbar$  only through  $E_0 \propto 1/\hbar^2$ . We shall see later, what is really meant when the foregoing phrase is used.

The many particle problem defined by Eqs. (7) and (8) cannot be solved exactly. It is much too complicated. This is true even when the number of electrons is only two, the situation of helium-like atoms. There is a branch of research<sup>3</sup> in which rigorous theorems about the system (7) and (8) are proved, such as (disappointingly rough) limits on the total binding energy. One can show for example, that for  $N=Z \rightarrow \infty$  the many particle problem reduces to the original TF model, which we shall describe in the next Chapter. In these lectures, we shall not follow those highly mathematized lines. I prefer rather simple physical arguments instead of employing the machinery of functional analysis. Also, it is my impression that those "rigorous" methods are of little help when it comes to improving the description by going beyond the original TF model. Finally, let us not forget that mathematical theorems about (7) and (8) are not absolute knowledge about real atoms, because in putting down the Hamilton operator (7) we have already made physical approximations: the finite size and mass of the nucleus is disregarded; so are all relativistic effects including magnetic interactions and quantum electrodynamical corrections; other than electric interactions are neglected - no reference is made to gravitational and weak forces. Of course, both attitudes, the highly mathematical one and the more physical one, are valuable, but there is danger in judging one by the standards of the other.

Bohr atoms. We continue the introductory remarks by studying a very simple model in order to illustrate a few basic concepts. This primitive theoretical model neglects the inter-electronic interaction, thus treating the electrons as independently bound by the nucleus. But even if fermions do not interact they are aware of each other through the Pauli principle. Therefore, such noninteracting electrons (NIE) will fill the successive Bohr shells of the Coulomb potential with two electrons in each occupied orbital state.

For the present purpose it would be sufficient to consider the situation of  $m$  full Bohr shells. But with an eye on a later discussion of shell effects, in Chapter Five, let us additionally suppose

that the  $(m+1)$ th shell is filled by a fraction  $\mu$ ,  $0 \leq \mu < 1$ . Since the multiplicity of the shell with principal quantum number  $m'$  is  $2m'^2$ -fold, the total number,  $N$ , of electrons then is (see Problem 1)

$$\begin{aligned}
 N &= \sum_{m'=1}^m 2m'^2 + \mu 2(m+1)^2 & (1-9) \\
 &= \frac{2}{3} \left(m + \frac{1}{2}\right)^3 - \frac{1}{6} \left(m + \frac{1}{2}\right) + 2\mu(m+1)^2 \quad .
 \end{aligned}$$

The total binding energy for a nucleus of charge  $Z$  is even simpler,

$$\begin{aligned}
 -E &= \sum_{m'=1}^m 2m'^2 \frac{Z^2}{2m'^2} + \mu 2(m+1)^2 \frac{Z^2}{2(m+1)^2} & (1-10) \\
 &= Z^2(m+\mu) \quad ,
 \end{aligned}$$

which uses the single particle binding energy  $Z^2/(2m'^2)$ . If we understand Eq. (9) as defining  $m$  and  $\mu$  as functions of  $N$ , then Eq. (10) displays  $-E(Z, N)$ . Towards the objective of making this functional dependence explicit we proceed from noting that

$$\left(m + \frac{1}{2}\right)^3 - \frac{1}{4} \left(m + \frac{1}{2}\right) \leq \frac{3}{2}N < \left(m + \frac{3}{2}\right)^3 - \frac{1}{4} \left(m + \frac{3}{2}\right) \quad . \quad (1-11)$$

Consequently, if  $y$  solves the equation

$$y^3 - \frac{1}{4}y = \frac{3}{2}N \quad , \quad (1-12)$$

then  $m$  is the integer part of  $y - \frac{1}{2}$ . (For  $N > 0$ , there is just one solution larger than  $1/2$ .) We use the standard Gaussian notation,

$$m = [y - 1/2] \quad . \quad (1-13)$$

For the sequel the introduction of  $\langle y \rangle$ , defined by

$$\langle y \rangle = y - [y + 1/2] \quad , \quad (1-14)$$

that is

$$y - \langle y \rangle = \text{integer} \quad ,$$

$$-\frac{1}{2} \leq \langle y \rangle < \frac{1}{2} \quad , \quad (1-15)$$

will prove useful. We employ it in writing

$$m = y - 1 - \langle y - 1 \rangle = y - 1 - \langle y \rangle \quad . \quad (1-16)$$

The latter equality is based upon the obvious periodicity of  $\langle y \rangle$ ,

$$\langle y + 1 \rangle = \langle y \rangle \quad . \quad (1-17)$$

We can now insert both Eq.(12) and Eq.(15) into Eq.(9),

$$\begin{aligned} \frac{2}{3}(y^3 - \frac{1}{4}y) &= \frac{2}{3}(y - \frac{1}{2} - \langle y \rangle)^3 - \frac{1}{6}(y - \frac{1}{2} - \langle y \rangle) \\ &\quad + 2\mu(y - \langle y \rangle)^2 \quad , \end{aligned} \quad (1-18)$$

and solve for  $\mu$ . The result is

$$\mu = \frac{1}{2} + \langle y \rangle + (\langle y \rangle^2 - \frac{1}{4}) \frac{y - \frac{2}{3}\langle y \rangle}{(y - \langle y \rangle)^2} \quad . \quad (1-19)$$

As a consequence of  $y > \frac{1}{2}$ , the denominator here is nonzero. Also, one easily checks that, as  $y$  increases from  $m + \frac{1}{2}$  to  $m + \frac{3}{2}$ ,  $\mu$  grows monotonically from zero to one, as it should.

The combination of Eqs.(10), (16), and (19) now produces

$$-E = z^2 \left\{ y - \frac{1}{2} + (\langle y \rangle^2 - \frac{1}{4}) \frac{y - \frac{2}{3}\langle y \rangle}{(y - \langle y \rangle)^2} \right\} \quad , \quad (1-20)$$

with  $y(N)$  from Eq.(12). Let us first observe that this binding energy is a continuous function of  $y$  - and therefore of  $N$  - although  $\langle y \rangle$  occasionally jumps from  $+\frac{1}{2}$  to  $-\frac{1}{2}$ . Next, we note that for large  $N$ , Eq.(12) is solved by

$$y(N) = \left(\frac{3}{2}N\right)^{1/3} + \frac{1}{12} \left(\frac{3}{2}N\right)^{-1/3} + \dots \quad , \quad (1-21)$$

so that the oscillatory contribution in (20) is of order  $N^{-1/3}$ . Consequently, the binding energy of NIE is

$$-E = z^2 \left\{ \left(\frac{3}{2}N\right)^{1/3} - \frac{1}{2} + \dots \right\} \quad , \quad (1-22)$$

where the ellipsis indicates oscillatory terms of order  $N^{-1/3}$  and smal-

ler. The physical origin of these terms is the process of the filling of shells. We shall disregard them here with the promise of returning later when we shall engage in a more detailed discussion of shell effects.

Expansion (21) is expected to be good for large  $N$ . However, just the two terms displayed explicitly form a practically perfect formula even for small  $N$ . An impressive way of demonstrating the high quality of this two-term approximation is to look at the values predicted for  $N$ , at which closed shells occur. For  $Y = \frac{3}{2}, \frac{5}{2}, \frac{7}{2}, \dots$ , the exact answer of Eq. (12) is  $N=2, 10, 28, \dots$ , whereas Eq. (21) produces  $N=1.99987, 9.999974, 27.999991, \dots$ ; even for the first shell the agreement is better than one hundredth of a percent.

We have just learned an important lesson: a few terms of an asymptotic expansion like Eq. (21) may be, and frequently are, a highly accurate approximation even for very moderate values of  $N$ . Such considerations based upon large numbers are the origin of the label "statistical" that is attached to TF theory. The fundamental physical approximation is, however, rather a semiclassical one.

This will become clearer when we now answer the question how one can find the leading term in (22) somewhat more directly, without utilizing our detailed knowledge of the energy and degeneracy of bound states in the Coulomb potential.

The count of electrons is evaluated in Eq. (9) as the sum of the multiplicities of all occupied shells. Equivalently, we could have summed over all occupied states,

$$N = \sum_{\text{all states}} \left\{ \begin{array}{l} 1 \text{ if the state is occupied} \\ 0 \text{ if the state is not occupied} \end{array} \right\} . \quad (1-23)$$

Since a given state is occupied (or not) if its binding energy,  $-E_{\text{state}}$ , is larger than a certain amount,  $\zeta$ , (or less), we can employ Heaviside's unit step function,

$$\eta(x) = \begin{cases} 1 & \text{for } x > 0 \\ 0 & \text{for } x < 0 \end{cases} , \quad (1-24)$$

in writing

$$N(\zeta) = \sum_{\text{all states}} \eta(-E_{\text{state}} - \zeta) . \quad (1-25)$$

Such a sum over all eigenstates of an operator, here the single-particle Hamilton operator for NIE,

$$H_{\text{NIE}} = \frac{1}{2}p^2 - \frac{Z}{r} \quad , \quad (1-26)$$

is more concisely expressed as a trace. We then have

$$N(\zeta) = \text{tr} \eta(-H_{\text{NIE}} - \zeta) \quad . \quad (1-27)$$

[Do not worry about the possibility of partly filled shells. Then  $\zeta$  equals the binding energy of the respective shell, and the freedom of assigning any value between 0 and 1 to  $\eta(x=0)$  enables us to describe the situation of a fractionally filled shell. More about this in Chapter Five.] Analogously, we can express the energy of Eq.(10) as the sum over the single-particle energies of all occupied states,

$$E(\zeta) = \text{tr} H_{\text{NIE}} \eta(-H_{\text{NIE}} - \zeta) \quad . \quad (1-28)$$

The identity

$$\frac{d}{dx} (x \eta(x)) = \eta(x) \quad , \quad (1-29)$$

used in the form

$$- \int_x^\infty dx' \eta(-x') = x \eta(-x) \quad , \quad (1-30)$$

can be used to relate  $E(\zeta)$  to  $N(\zeta)$ :

$$\begin{aligned} E(\zeta) &= \text{tr} (H_{\text{NIE}} + \zeta) \eta(-H_{\text{NIE}} - \zeta) - \zeta \text{tr} \eta(-H_{\text{NIE}} - \zeta) \\ &= - \text{tr} \int_\zeta^\infty d\zeta' \eta(-H_{\text{NIE}} - \zeta') - \zeta N(\zeta) \quad , \end{aligned} \quad (1-31)$$

or,

$$E(\zeta) = - \zeta N(\zeta) - \int_\zeta^\infty d\zeta' N(\zeta') \quad . \quad (1-32)$$

We see that  $E(\zeta)$  is immediately available as soon as we know  $N(\zeta)$ . This is no surprise. Recall that  $N(\zeta)$  signifies the number of states with binding energy larger than  $\zeta$ . Consequently,  $N(\zeta)$  is discontinuous at all values of  $\zeta$  equal to the binding energy of a (Bohr) shell, and the size

of the jump of  $N(\zeta)$  at such a discontinuity is the multiplicity of the respective shell. So  $N(\zeta)$ , regarded as a function of  $\zeta$ , tells us both the energy and the multiplicity of all shells.

The problem is now reduced to evaluating the trace in Eq. (27) in an appropriate, approximate way. [Remember, it is the leading term of Eq. (22) only, that we want to derive simply.] First an intuitive argument. The count of states is the spin multiplicity of two, times the count of orbital states. There is roughly one orbital state per phase-space volume  $(2\pi\hbar)^3$  [ $= (2\pi)^3$  in atomic units], so that

$$N(\zeta) \cong 2 \int \frac{(d\vec{r}') (d\vec{p}')}{(2\pi)^3} \eta\left(-\left(\frac{1}{2}p'^2 - \frac{Z}{r'}\right) - \zeta\right) , \quad (1-33)$$

where primes have been used to distinguish numbers from operators. The step function equals unity in the classically allowed domain of the phase-space and vanishes outside. Therefore, Eq. (33) represents the extreme semiclassical (or should we say: semiquantal?) limit, in which the possibility of finding the quantum-mechanical system outside the classical allowed region is ignored.

Some support for the approximation (33) is supplied by its implications. After performing the momentum integration, we have

$$N(\zeta) \cong \int (d\vec{r}') \frac{1}{3\pi^2} \left[2\left(\frac{Z}{r'} - \zeta\right)\right]^{3/2} , \quad (1-34)$$

where the square root is understood to vanish for negative arguments. Then the  $r'$  integration produces, with  $x = \zeta r'/Z$ ,

$$\begin{aligned} N(\zeta) &\cong (2Z^2/\zeta)^{3/2} \frac{4}{3\pi} \int_0^1 dx x^{1/2} (1-x)^{3/2} \\ &= \frac{2}{3} \left(\frac{Z^2}{2\zeta}\right)^{3/2} . \end{aligned} \quad (1-35)$$

(the integral has the value  $\pi/16$ .) Insertion into Eq. (32) results in

$$-E(\zeta) \cong Z^2 \left(\frac{Z^2}{2\zeta}\right)^{1/2} , \quad (1-36)$$

which combined with (35) is

$$-E \cong Z^2 \left(\frac{3}{2}N\right)^{1/3} . \quad (1-37)$$

Indeed, here is the leading term of Eq. (22), now very simply reproduced by the semiclassical counting of states. Please note that the steps from Eq. (32) to Eq. (37) did not require any knowledge about the energy and multiplicity of bound states in the Coulomb potential.

Traces and phase-space integrals. One does not have to rely upon intuition alone when writing down Eq. (33). A general way of evaluating the trace of a function of position operator  $\vec{r}$  and the conjugate momentum operator  $\vec{p}$  is

$$\begin{aligned} \text{tr } F(\vec{r}, \vec{p}) &= \int (d\vec{r}') \langle \vec{r}' | F(\vec{r}, \vec{p}) | \vec{r}' \rangle \\ &= \int (d\vec{r}') (d\vec{p}') \langle \vec{r}' | F(\vec{r}, \vec{p}) | \vec{p}' \rangle \langle \vec{p}' | \vec{r}' \rangle . \end{aligned} \quad (1-38)$$

We have left out the factor of two for the spin multiplicity here, because it is irrelevant for the present discussion. If now  $F(\vec{r}, \vec{p})$  is ordered such that all  $\vec{r}$ 's stand to the left of all  $\vec{p}$ 's, then

$$\langle \vec{r}' | F(\vec{r}, \vec{p}) | \vec{p}' \rangle = F(\vec{r}', \vec{p}') \langle \vec{r}' | \vec{p}' \rangle . \quad (1-39)$$

This, combined with the position-momentum transformation functions

$$\begin{aligned} \langle \vec{r}' | \vec{p}' \rangle &= \frac{1}{(2\pi)^{3/2}} e^{i \vec{r}' \cdot \vec{p}'} , \\ \langle \vec{p}' | \vec{r}' \rangle &= \frac{1}{(2\pi)^{3/2}} e^{-i \vec{r}' \cdot \vec{p}'} , \end{aligned} \quad (1-40)$$

and inserted into (38) produces

$$\text{tr } F(\vec{r}, \vec{p}) = \int \frac{(d\vec{r}') (d\vec{p}')}{(2\pi)^3} F(\vec{r}', \vec{p}') \quad (1-41)$$

Equation (41) is an exact statement for an ordered operator  $F(\vec{r}, \vec{p})$ . If the operator, of which the trace is desired, is not ordered, one can sometimes do the ordering explicitly. An example is (see Problem 3)

$$e^{-i(\frac{1}{2}\vec{p}^2 - \vec{p} \cdot \vec{r})t} =$$

$$= e^{i \vec{F} \cdot \vec{r} t} e^{-i \frac{1}{2} (\vec{p} + \frac{1}{2} \vec{F} t)^2 t} e^{-i F^2 t^3 / 24} \quad (1-42)$$

where  $\vec{F}$  is a constant vector. With the aid of (42), all other functions of  $\frac{1}{2} \vec{p}^2 - \vec{F} \cdot \vec{r}$  can be ordered if expressed as the appropriate Fourier integral. We shall have a use for Eq. (42) later, in Chapter Four.

With the exception of a few relatively simple instances, the ordering of an operator  $F(\vec{r}, \vec{p})$  is practically impossible. However, even then Eq. (41) is not useless. Inasmuch as the ordering process involves the evaluation of commutators of functions of  $\vec{r}$  with functions of  $\vec{p}$ ,  $\langle \vec{r}' | F(\vec{r}, \vec{p}) | \vec{p}' \rangle$  differs from  $F(\vec{r}', \vec{p}') \langle \vec{r}' | \vec{p}' \rangle$  by commutator terms. Under circumstances when these commutators are small,

$$\text{tr } F(\vec{r}, \vec{p}) \approx \int \frac{(d\vec{r}') (d\vec{p}')}{(2\pi)^3} F(\vec{r}', \vec{p}') \quad (1-43)$$

can be used as the basis for approximations. Since the noncommutativity of  $\vec{r}$  and  $\vec{p}$  becomes insignificant in the semiclassical limit, Eq. (43) manifests a highly semiclassical approximation.

All refinements of (43) are due to the noncommutativity of position and momentum. This is at the heart of quantum mechanics, and we shall therefore call these improvements "quantum corrections," notwithstanding the fact that (41) is already a quantum mechanical result. The starting point is clearly the semiclassical (or, semiquantal) picture, not the classical theory of the atom, which does not exist in the first place.

For the trace of Eq. (27) all this means that the semiclassical evaluation of Eq. (33) will be a reliable approximation, if the de-Broglie wavelength of an individual electron is small compared to the typical distance over which the Coulomb potential varies significantly. This condition is satisfied if both the number of electrons and the nuclear charge are large, because in this situation the electronic cloud is very dense. In this sense the semiclassical approximation is equivalent to a large- $N$ , a statistical one.

Bohr atoms with shielding. The primitive model of NIE constitutes a sensible approximation for highly ionized atoms only, in which the dynamics is governed by the Coulomb potential of the nucleus, and the electron-electron interaction is negligible. Consequently, the results obtained above should not be taken seriously, unless  $N \ll Z$ . For instance, the

binding energy of a neutral atom is expected to differ significantly from the prediction of Eq. (37),

$$-E \approx \left(\frac{3}{2}\right)^{1/3} Z^{7/3} = 1.145 Z^{7/3} \quad , \quad (1-44)$$

because of the screening of the nuclear Coulomb potential by the inner shells. Let us, therefore, try to get a feeling for the importance of the electron-electron interactions by refining the NIE picture.

Without inner-shell screening, each full Bohr shell contributes the amount of  $Z^2$  to the binding energy [see Eq. (10)]. We now suppose that this remains true for the first shell, whereas the effective  $Z$ -value for the second shell is  $Z-2$ , since the total charge of the nucleus together with the first shell is  $(-Z+2)e$ . Similarly, the third shell sees  $Z-2-8=Z-10$ , and so on. In this picture,<sup>4</sup> the screening of the inner shells is so effective that the  $m'$ -th shell is exposed to a Coulomb potential  $-Z_{m'}/r$  with

$$Z_{m'} = Z - \sum_{m''=1}^{m'-1} 2m''^2 \quad . \quad (1-45)$$

Its contribution to the binding energy is  $Z_{m'}^2$ , so that we have

$$-E = \sum_{m'=1}^m Z_{m'}^2 + \mu Z_{m+1}^2 \quad . \quad (1-46)$$

We are interested in the leading term only and can, therefore, evaluate the various sums over  $m'$  by means of

$$\sum_{m'=1}^m m'^{\nu} \approx \frac{1}{\nu+1} m^{\nu+1} \quad . \quad (1-47)$$

We can then also disregard all effects of the filling of shells, since the terms proportional to  $\mu$  are of a lower order, both in  $N$  [Eq. (9)] and in  $E$ . To leading order, we have

$$N \approx \frac{2}{3} m^3 \quad , \quad (1-48)$$

$$Z_{m'} \approx Z - \frac{2}{3} (m'-1)^3 \quad ,$$

as well as

$$\begin{aligned}
 -E &= \sum_{m'=1}^m Z^2_{m'} \cong \sum_{m'=1}^m [Z - \frac{2}{3}(m'-1)]^2 \\
 &\cong Z^2 m - \frac{1}{3} Z m^4 + \frac{4}{63} m^7 \quad ,
 \end{aligned}
 \tag{1-49}$$

or,

$$\begin{aligned}
 -E &= Z^2 (\frac{3}{2}N)^{1/3} - \frac{1}{3} Z (\frac{3}{2}N)^{4/3} + \frac{4}{63} (\frac{3}{2}N)^{7/3} \\
 &= Z^2 (\frac{3}{2}N)^{1/3} [1 - \frac{1}{2} \frac{N}{Z} + \frac{1}{7} (\frac{N}{Z})^2] \quad .
 \end{aligned}
 \tag{1-50}$$

For neutral atoms,  $N = Z$ , the prediction for the total binding energy is now

$$\begin{aligned}
 -E &\cong (1 - \frac{1}{2} + \frac{1}{7}) Z^2 (\frac{3}{2}Z)^{1/3} \\
 &= \frac{9}{14} (\frac{3}{2})^{1/3} Z^{7/3} = 0.736 Z^{7/3} \quad .
 \end{aligned}
 \tag{1-51}$$

The comparison with (44) shows that the inner-shell screening reduces the total binding energy by roughly one third. It certainly is a substantial effect in a neutral atom.

Incidentally, it is remarkable that the numerical coefficient in (51) differs from the correct answer (see the next Chapter) by less than 5%. In view of the crude way, in which the electron-electron interaction has been taken into account, this is much better than one could possibly expect.

The effective potential. The model that we just studied possesses one particularly unsatisfactory feature: the inner shells influence the outer ones, but not vice versa. There is action but no reaction - hardly a good way of describing interaction.

In our present, preliminary attempt of resolving this insufficiency, in the framework of a modified Bohr model, we shall continue to assume that the various Bohr shells are geometrically separated. The  $m'$ -th shell is supposed to be spherical of a certain radius,  $R_{m'}$ . Then the potential energy of an electron with this shell is

$$U_{m'}(r) = \begin{cases} 2m'^2/R_{m'} & \text{for } r < R_{m'} \\ 2m'^2/r & \text{for } r > R_{m'} \end{cases} \quad ,
 \tag{1-52}$$

if the electron is situated at a distance  $r$  from the nucleus. The picture is no longer asymmetric now, since the energy of the  $m''$ -th shell in the electrostatic field of the  $m'$ -th shell,

$$2m''^2 U_{m'}(R_{m''}) = (2m''^2)(2m'^2)/\text{Max}(R_{m'}, R_{m''}) \quad , \quad (1-53)$$

remains unaltered if  $m'$  and  $m''$  are interchanged; action and reaction are equal.

The total potential energy of the electrons in the  $m'$ -th Bohr shell is the sum of the potential energy with the nucleus and with all other shells,

$$E_{\text{pot},m'} = 2m'^2 \left[ -\frac{Z}{R_{m'}} + \sum_{m''=1}^m \frac{1}{m''} U_{m''}(R_{m'}) + \mu U_{m+1}(R_{m'}) \right] \quad . \quad (1-54)$$

In this sum, the prime is a reminder to delete the term with  $m''=m'$ . Including this term would mean to include the self energy of the  $m'$ -th shell. This is not undesirable, though, because the self energy of the shell consists mostly of the interaction energy of the individual electrons in the shell. The unphysical electron self-energy can be expected to be a relatively small fraction of the shell self-energy. Thus we feel justified in dropping the prime on the sum in (54), implying

$$E_{\text{pot},m'} = 2m'^2 V(R_{m'}) \quad , \quad (1-55)$$

which introduces the effective potential

$$V(r) = -\frac{Z}{r} + \sum_{m'=1}^m \frac{1}{m'} U_{m'}(r) + \mu U_{m+1}(r) \quad . \quad (1-56)$$

It is the same for all shells, i.e. for all electrons.

Before going on, let us supply additional evidence in favor of the introduction of the effective potential. It comes from evaluating the total self energy of all shells. This is

$$\begin{aligned} E_{\text{sse}} &= \frac{1}{2} \sum_{m'=1}^m 2m'^2 U_{m'}(R_{m'}) + \frac{1}{2} \mu (2(m+1)^2) \mu U_{m+1}(R_{m+1}) \\ &= \frac{1}{2} \sum_{m'=1}^m \frac{(2m'^2)^2}{R_{m'}} + \frac{1}{2} \frac{\mu^2 (2(m+1)^2)^2}{R_{m+1}} \quad ; \end{aligned} \quad (1-57)$$

the subscript sse stands for same-shell electrons. It now becomes necessary to specify the radii of the shells,  $R_{m'}$ . An electron of the  $m'$ -th shell moves in a potential of the form  $-Z_{m'}/r + \text{const}$ . This is, besides the here irrelevant additive constant, a Coulomb potential. Consequently, the expectation values of the kinetic and potential energy of this electron are  $Z_{m'}^2/(2m'^2)$  and  $-Z_{m'}^2/m'^2 + \text{const}$ , respectively. It is natural to define  $R_{m'}$  by equating this potential-energy expectation-value to  $-Z_{m'}/R_{m'} + \text{const}$ . This means

$$\frac{Z_{m'}^2}{m'^2} = \frac{Z_{m'}}{R_{m'}} \quad , \quad (1-58)$$

or,

$$\frac{m'^2}{R_{m'}} = Z_{m'} = Z - \sum_{m''=1}^{m'-1} 2m''^2 \quad ; \quad (1-59)$$

the latter equality is Eq.(45). (Of course, no claims are made that this represents the one and only way of defining  $R_{m'}$ . The electrons of a Bohr shell are not geometrically confined to a small range of  $r$ , so that there cannot be a unique, physical value ascribed to  $R_{m'}$ .)

Upon inserting (59) into (57), we have

$$\begin{aligned} E_{\text{sse}} &= \sum_{m'=1}^m 2m'^2 Z_{m'} + \mu^2 2(m+1)^2 Z_{m+1} \\ &= \sum_{m'=1}^m 2m'^2 \left[ Z - \frac{2}{3} \left(m' - \frac{1}{2}\right)^3 + \frac{1}{6} \left(m' - \frac{1}{2}\right) \right] \\ &\quad + \mu^2 2(m+1)^2 \left[ Z - \frac{2}{3} \left(m + \frac{1}{2}\right)^3 + \frac{1}{6} \left(m + \frac{1}{2}\right) \right] \quad , \end{aligned} \quad (1-60)$$

of which the leading terms are [Eqs.(47) and (48)]

$$\begin{aligned} E_{\text{sse}} &\cong \frac{2}{3} Z m^3 - \frac{2}{9} m^6 \\ &= Z^2 \left[ \frac{N}{Z} - \frac{1}{2} \left(\frac{N}{Z}\right)^2 \right] \quad . \end{aligned} \quad (1-61)$$

For a neutral atom ( $N/Z = 1$ ), this is

$$E_{\text{sse}} \cong \frac{1}{2} Z^2 \quad , \quad (1-62)$$

and does not contribute to the leading term of the binding energy, which is  $\sim Z^{7/3}$ .

Since the self energy of the  $m'$ -th shell is proportional to  $(2m')^2$ , i.e., to the square of the number of electrons it contains, whereas the sum of all electron self-energies is proportional to their number ( $2m'^2$  for those of the  $m'$ -th shell,  $N$  for the whole atom), the error made in the total binding energy by the inclusion of the electron self-energy is very small on the scale set by the leading term (proportional to  $Z^{7/3}$ ). Moreover, as soon as we shall have included the exchange interaction into the description, the electronic self energy will be exactly cancelled by the equally unphysical self-exchange energy. In other words: there is no reason at all to worry about the self energy; at the present stage it does not contribute significantly, and later it is going to be taken care of automatically.

In the effective potential, the use of which now being justified, the electrons move independently. As the main consequence, the complicated many-particle problem is reduced to an effective single-particle one. In our present model the total kinetic energy is

$$E_{\text{kin}} = \sum_{m'=1}^m Z_{m'}^2 + \mu Z_{m+1}^2 \quad (1-63)$$

[recall, once more, that the kinetic energy of an electron in a Coulomb potential  $-Z_{m'}/r + \text{const}$ , as is the situation in the  $m'$ -th shell, is given by  $Z_{m'}^2/(2m'^2)$ ]. Further, the independent-particle (IP) potential energy can be expressed with the aid of the effective potential  $V$ ,

$$E_{\text{IP,pot}} = \sum_{m'=1}^m 2m'^2 V(R_{m'}) + \mu 2(m+1)^2 V(R_{m+1}) \quad (1-64)$$

Together they constitute an approximation to the independent-particle energy  $E_{\text{IP}}$ :

$$E_{\text{IP}} = E_{\text{kin}} + E_{\text{IP,pot}} \quad (1-65)$$

$$= \sum_{m'=1}^m Z_{m'}^2 + \sum_{m'=1}^m 2m'^2 V(R_{m'}) + \mu [Z_{m+1}^2 + 2(m+1)^2 V(R_{m+1})] .$$

This is, however, not the energy of the system. Because of the use of the effective potential, the electron-electron interaction is counted twice in (65). In addition to the energy of the  $m'$ -th shell in the elec-

trostatic field of the  $m''$ -th shell,  $2m'^2 U_{m''}(R_{m'})$ ,  $E_{IP}$  also contains  $2m''^2 U_{m'}(R_{m''})$ , for any pair  $m', m''$ ; and the two are equal, as we have seen earlier, in Eq. (53). Consequently, we have to remove the electron-electron interaction energy once. This is conveniently achieved by expressing this energy in terms of the electric field made by the electrons,

$$\vec{E} = - \vec{\nabla} \left( V - \left( -\frac{Z}{r} \right) \right) \quad . \quad (1-66)$$

We have carefully subtracted the contribution to  $V$  that stems from the nuclear charge. What we have to add to  $E_{IP}$  in order to remove the doubly counted interaction energy, is then

$$\begin{aligned} E_2 &= - \frac{1}{8\pi} \int (d\vec{r}) \vec{E}^2 \\ &= - \frac{1}{8\pi} \int (d\vec{r}) \left[ \vec{\nabla} \left( V + \frac{Z}{r} \right) \right]^2 \quad . \end{aligned} \quad (1-67)$$

The evaluation of this integral is facilitated by the observation that in our model

$$V(r) + \frac{Z}{r} = \frac{Z - Z_{m'+1}}{r} + \text{const} \quad \text{for } R_{m'} < r < R_{m'+1} \quad . \quad (1-68)$$

Accordingly,

$$\left[ \vec{\nabla} \left( V + \frac{Z}{r} \right) \right]^2 = \frac{(Z - Z_{m'+1})^2}{r^4} \quad \text{for } R_{m'} < r < R_{m'+1} \quad , \quad (1-69)$$

which holds for  $m' = 1, 2, \dots, m$ . Additionally, we need

$$\left[ \vec{\nabla} \left( V + \frac{Z}{r} \right) \right]^2 = \begin{cases} 0 & \text{for } r < R_1 \\ \frac{N^2}{r^4} & \text{for } r > R_{m+1} \end{cases} \quad . \quad (1-70)$$

At this stage, we have

$$E_2 = - \frac{1}{8\pi} \left[ \int_0^{R_1} + \int_{R_1}^{R_2} + \dots + \int_{R_m}^{R_{m+1}} + \int_{R_{m+1}}^{\infty} \right] 4\pi r^2 dr \left[ \vec{\nabla} \left( V + \frac{Z}{r} \right) \right]^2 =$$

$$\begin{aligned}
&= -\frac{1}{2} \sum_{m'=1}^m \int_{R_{m'}}^{R_{m'+1}} dr \frac{(Z-Z_{m'+1})^2}{r^2} - \frac{1}{2} \int_{R_{m+1}}^{\infty} dr \frac{N^2}{r^2} \quad (1-71) \\
&= -\frac{1}{2} \sum_{m'=1}^m (Z-Z_{m'+1})^2 \left( \frac{1}{R_{m'}} - \frac{1}{R_{m'+1}} \right) - \frac{1}{2} \frac{N^2}{R_{m+1}} .
\end{aligned}$$

A unit shift of the summation index transforms the sum with  $R_{m'+1}$  into an equivalent one with  $R_{m'}$ :

$$E_2 = -\frac{1}{2} \sum_{m'=1}^m \frac{(Z-Z_{m'+1})^2}{R_{m'}} + \frac{1}{2} \sum_{m'=2}^{m+1} \frac{(Z-Z_{m'})^2}{R_{m'}} - \frac{1}{2} \frac{N^2}{R_{m+1}} . \quad (1-72)$$

The recognition that  $Z - Z_1 = 0$ , combined with

$$\begin{aligned}
&(Z-Z_{m'+1})^2 - (Z-Z_{m'})^2 \\
&= (Z_{m'} - Z_{m'+1}) [(Z-Z_{m'}) + (Z-Z_{m'+1})] \\
&= 2m'^2 \left( 2 \sum_{m''=1}^{m'-1} 2m''^2 + 2m'^2 \right) \\
&= 2m'^2 R_{m'} \left( 2 \sum_{m''=1}^{m'-1} U_{m''}(R_{m'}) + U_{m'}(R_{m'}) \right) , \quad (1-73)
\end{aligned}$$

which uses Eqs.(45) and (52), as well as [Eqs.(45), (52) and (9)]

$$\begin{aligned}
N^2 - (Z-Z_{m+1})^2 &= \mu 2(m+1)^2 \left[ 2 \sum_{m''=1}^m 2m''^2 + \mu 2(m+1)^2 \right] \\
&= \mu 2(m+1)^2 R_{m+1} \left( 2 \sum_{m''=1}^m U_{m''}(R_{m+1}) + \mu U_{m+1}(R_{m+1}) \right) , \quad (1-74)
\end{aligned}$$

turns (72) into

$$E_2 = - \left\{ \sum_{m'=1}^m 2m'^2 \sum_{m''=1}^{m'-1} U_{m''}(R_{m'}) + \mu 2(m+1)^2 \sum_{m''=1}^m U_{m''}(R_{m+1}) \right\} - \quad (1-75)$$

$$- \left\{ \frac{1}{2} \sum_{m'=1}^m 2m'^2 U_{m'}(R_{m'}) + \frac{1}{2} [\mu 2(m+1)^2] [\mu U_{m+1}(R_{m+1})] \right\} .$$

The contents of the two curly brackets are immediately recognized as the interaction energy of the pairs of shells and the self energy  $E_{\text{sse}}$  of the individual shells, respectively. Indeed,  $E_2$  is the negative of the electron-electron interaction energy, as it should be.

Before adding  $E_{\text{IP}}$  of (65) and  $E_2$  of (75) to get the total energy itself, it is useful to rewrite  $E_{\text{IP,pot}}$ . From (64) we get

$$\begin{aligned} E_{\text{IP,pot}} &= \sum_{m'=1}^m 2m'^2 \left[ -\frac{Z}{R_{m'}} + \sum_{m''=1}^m U_{m''}(R_{m'}) + \mu U_{m+1}(R_{m'}) \right] \\ &+ \mu 2(m+1)^2 \left[ -\frac{Z}{R_{m+1}} + \sum_{m'=1}^m U_{m'}(R_{m+1}) + \mu U_{m+1}(R_{m+1}) \right] \\ &= \sum_{m'=1}^m \frac{2m'^2}{R_{m'}} (-Z + \sum_{m''=1}^{m'-1} 2m''^2) + \sum_{m'=1}^m 2m'^2 U_{m'}(R_{m'}) \\ &+ \sum_{m'=1}^m \sum_{m''=m'+1}^m 2m'^2 U_{m''}(R_{m'}) \tag{1-76} \\ &+ \mu \sum_{m'=1}^m 2m'^2 U_{m+1}(R_{m'}) \\ &+ \mu \frac{2(m+1)^2}{R_{m+1}} (-Z + \sum_{m'=1}^m 2m'^2) \\ &+ [\mu 2(m+1)^2] \times [\mu U_{m+1}(R_{m+1})] . \end{aligned}$$

After using Eq.(59) and the  $m'$ - $m''$  symmetry of  $2m'^2 U_{m''}(R_{m'})$  [the action-reaction symmetry that we observed in Eq.(53)], this reads

$$\begin{aligned} E_{\text{IP,pot}} &= -2 \sum_{m'=1}^m Z^2_{m'} - 2\mu Z^2_{m+1} \\ &+ \left\{ \sum_{m''=1}^m \sum_{m'=1}^{m''-1} 2m''^2 U_{m'}(R_{m''}) + \mu (2m+1)^2 \sum_{m'=1}^m U_{m'}(R_{m+1}) \right\} + \end{aligned}$$

$$\begin{aligned}
& + 2 \left\{ \frac{1}{2} \sum_{m'=1}^m 2m'^2 U_{m'}(R_{m'}) + \frac{1}{2} [\mu 2(m+1)^2] [\mu U_{m+1}(R_{m+1})] \right\} \\
& = - 2 \sum_{m'=1}^m Z_{m'}^2 - 2\mu Z_{m+1}^2 - E_2 + E_{sse} \quad . \quad (1-77)
\end{aligned}$$

Finally, we obtain the total binding energy

$$-E = - (E_{kin} + E_{IP,pot} + E_2) \quad (1-78)$$

$$= \sum_{m'=1}^m Z_{m'}^2 + \mu Z_{m+1}^2 - E_{sse} \quad .$$

We compare this with Eq.(46) and notice that the more symmetrical treatment of the electrons leads to an additional term,  $E_{sse}$ , in the energy. This is very satisfactory because  $E_{sse}$  is the interaction energy of electrons in the same shell (plus the innocuous electron self-energy), which was left out when (46) was derived.

Equation (78) can be simplified. First, we use

$$2m'^2 = Z_{m'} - Z_{m'+1} \quad (1-79)$$

and

$$\mu 2(m+1)^2 = Z_{m+1} - (Z-N) \quad , \quad (1-80)$$

which are consequences of Eqs.(45) and (9), to rewrite  $E_{sse}$  of (60) as

$$E_{sse} = \sum_{m'=1}^m (Z_{m'} - Z_{m'+1}) Z_{m'} + \mu Z_{m+1}^2 - \mu (Z-N) Z_{m+1} \quad . \quad (1-81)$$

Then we insert this into (78). The outcome is

$$-E = \sum_{m'=1}^m Z_{m'} Z_{m'+1} + \mu (Z-N) Z_{m+1} \quad . \quad (1-82)$$

We can now evaluate the sum over  $m'$ , express  $m$  and  $\mu$  in terms of  $y$ , as given in Eqs.(16) and (19), and pick out the two leading contributions to  $-E$ . They are

$$-E = (Z^2 y - \frac{1}{3} Z y^4 + \frac{4}{63} y^7) - \frac{1}{2} Z^2 + O(Z^{5/3} \sim Z y^2 \sim y^5) \quad (1-83)$$

To this order,  $y$  is simply given by  $(\frac{3}{2}N)^{1/3}$  [Eq.(21)], so that

$$-E = Z^2 (\frac{3}{2}N)^{1/3} (1 - \frac{1}{2} \frac{N}{Z} + \frac{1}{7} (\frac{N}{Z})^2) - \frac{1}{2} Z^2 + O(ZN^{2/3} \sim N^{5/3}) \quad (1-84)$$

The neutral-atom binding energy predicted by our improved model of Bohr atoms with shielding is, consequently,

$$-E = 0.736 Z^{7/3} - \frac{1}{2} Z^2 + O(Z^{5/3}) \quad (1-85)$$

Without shielding, that is: without accounting for the electron-electron interaction, the result was [Eq.(22) for  $N = Z$ ]

$$-E = 1.145 Z^{7/3} - \frac{1}{2} Z^2 + O(Z^{5/3}) \quad (1-86)$$

Whereas the screening of the nuclear potential by the inner electrons reduces the leading term by  $5/14 \approx 1/3$ , it does not affect the  $Z^2$  term at all. We shall see later, in Chapter Three, that this next-to-leading term is a consequence of the Coulomb shape of the effective potential for small  $r$ . It is the same for all potentials with  $V \approx -Z/r$  for  $r \rightarrow 0$ , for which reason it is independent of  $N$  [Eqs.(22) and (84) confirm this]. The two examples that we looked at so far, the Coulomb potential of (26) and the  $V(r)$  of (56), both have this property.

Size of atoms. A last application of our model of Bohr atoms with shielding consists in studying the  $Z$  dependence of the size of neutral atoms. The individual Bohr shells shrink proportional to  $1/Z_m$ , as  $Z$  increases [see Eq.(59)]. This would mean that the size of an atom is roughly given by  $1/Z$ , if there were not the necessity of filling additional shells to compensate for the growth of nuclear charge. Clearly, a qualified statement about atomic size requires the evaluation of some average of  $r$  over the atom.

According to Eq.(59), it is the inverse of  $R_m$ , that is easy to handle. We shall therefore measure the size  $R$  of an atom as

$$\frac{1}{R} = \frac{1}{N} \langle \frac{1}{r} \rangle \quad , \quad (1-87)$$

where  $\langle 1/r \rangle$  denotes the expectation value of  $1/r$ . In our model it is given by

$$\langle \frac{1}{r} \rangle = \sum_{m'=1}^m \frac{2m'^2}{R_{m'}} + \mu \frac{2(m+1)^2}{R_{m+1}} \quad . \quad (1-88)$$

It has a simple physical significance:  $\langle 1/r \rangle$  is the electrostatic energy of the electrons in the field of a unit charge situated at the location of the nucleus,  $r=0$ ; or, equivalently, the electrostatic energy of this unit charge in the field of the electrons. As such it can be evaluated in terms of the effective potential  $V$ :

$$\langle \frac{1}{r} \rangle = (V + \frac{Z}{r})(r=0) = \sum_{m'=1}^m U_{m'}(0) + \mu U_{m+1}(0) \quad . \quad (1-89)$$

Indeed, Eq.(52) assures us of the equivalence of (88) and (89).

After employing Eq.(59) to rewrite (88),

$$\begin{aligned} \langle \frac{1}{r} \rangle &= 2 \sum_{m'=1}^m Z_{m'} + 2\mu Z_{m+1} \\ &= 2 \sum_{m'=1}^m (Z - \frac{2}{3}m'(m'-1)(m' - \frac{1}{2})) + 2\mu(Z-N) + 4\mu^2(m+1)^2 \end{aligned} \quad (1-90)$$

[the latter equality also uses Eq.(80)], we can sum over  $m'$  and then identify the leading contributions with the aid of Eqs.(16), (19), and (21). The result is

$$\langle \frac{1}{r} \rangle = 2Z (\frac{3}{2}N)^{1/3} (1 - \frac{1}{4} \frac{N}{Z}) - Z (1 - \frac{N}{Z}) + O(N^{2/3} \sim ZN^{-1/3}) \quad , \quad (1-91)$$

which for neutral atoms reads

$$\langle \frac{1}{r} \rangle = (\frac{3}{2}Z)^{4/3} + O(Z^{2/3}) \quad . \quad (1-92)$$

Consequently, the atomic size is [Eq.(87)]

$$R \sim Z^{-1/3} . \quad (1-93)$$

Heavier atoms are geometrically smaller. This prediction of our rather simple model will remain valid in more realistic treatments.

A remarkable observation is the agreement of Eq. (92) with the Z derivative of Eq. (84) to leading order,

$$\langle \frac{1}{r} \rangle \approx \frac{\partial}{\partial Z} (-E) . \quad (1-94)$$

Its physical significance becomes transparent when we exhibit the change in the binding energy that is caused by increasing the nuclear charge Z by the infinitesimal amount  $\delta Z$ :

$$\delta(-E) = \frac{\partial}{\partial Z} (-E) \delta Z \approx \langle \frac{\delta Z}{r} \rangle . \quad (1-95)$$

This says that the change in the binding energy is mainly given by the electrostatic energy of the extra nuclear charge; the induced alterations of the shell radii  $R_m$ , do not contribute to  $\delta(-E)$  to leading order. This result of the model must be contrasted with the corresponding implication of the exact treatment based upon the many-particle Hamilton operator (7). In general, an infinitesimal change of a parameter in a Hamilton operator causes a change in the energy, which is equal to the expectation value of the respective change of the Hamilton operator<sup>5</sup>. In the present discussion, this statement reads

$$\delta(-E) = \langle \delta(-H_{mp}) \rangle = \langle \sum_j \frac{\delta Z}{r_j} \rangle = \langle \frac{\delta Z}{r} \rangle , \quad (1-96)$$

which says that the change in the binding energy is entirely given by the electrostatic energy of the extra nuclear charge  $\delta Z$ .

As we see, in our model of Bohr atoms with shielding, Eq. (96) is not obeyed exactly, but approximately. This minor deficiency could possibly be removed by a slightly different definition of the  $R_m$ , [Eq. (59)]. It is not worth the trouble, though.

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The models studied in this Introduction not only provided a first insight into the general characteristics of complex atoms, but also made us somewhat familiar with a few important ideas: the concept of the effective potential, the semiclassical evaluation of traces through phase-space integrals, and relations of the kind illustrated by Eq. (32) are the central ones. The next Chapter, devoted to the Tho-

mas-Fermi model, will use them for a first self-consistent description.

### Problems

1-1. Sums of powers of  $m'$ , as, e.g., in Eq.(9), can be conveniently evaluated following the pattern of this example:

$$\begin{aligned} \sum_{m'=1}^m m' &= \sum_{m'=1}^m \frac{1}{2} [(m' + \frac{1}{2})^2 - (m' - \frac{1}{2})^2] \\ &= \frac{1}{2} \sum_{m'=1}^m (m' + \frac{1}{2})^2 - \frac{1}{2} \sum_{m'=0}^{m-1} (m' + \frac{1}{2})^2 \\ &= \frac{1}{2} (m + \frac{1}{2})^2 - \frac{1}{2} (0 + \frac{1}{2})^2 = \frac{1}{2} (m + \frac{1}{2})^2 - \frac{1}{8} \quad . \end{aligned}$$

Show that the other sums, that occur in this Chapter, are given by

$$\sum_{m'=1}^m m'^2 = \frac{1}{3} (m + \frac{1}{2})^3 - \frac{1}{12} (m + \frac{1}{2}) \quad ,$$

$$\sum_{m'=1}^m m'^3 = \frac{1}{4} (m + \frac{1}{2})^4 - \frac{1}{8} (m + \frac{1}{2})^2 + \frac{1}{64} \quad ,$$

$$\sum_{m'=1}^m m'^4 = \frac{1}{5} (m + \frac{1}{2})^5 - \frac{1}{6} (m + \frac{1}{2})^3 + \frac{7}{240} (m + \frac{1}{2}) \quad ,$$

$$\sum_{m'=1}^m m'^5 = \frac{1}{6} (m + \frac{1}{2})^6 - \frac{5}{24} (m + \frac{1}{2})^4 + \frac{7}{96} (m + \frac{1}{2})^2 - \frac{1}{128} \quad ,$$

and

$$\sum_{m'=1}^m m'^6 = \frac{1}{7} (m + \frac{1}{2})^7 - \frac{1}{4} (m + \frac{1}{2})^5 + \frac{7}{48} (m + \frac{1}{2})^3 - \frac{31}{1344} (m + \frac{1}{2}) \quad .$$

1-2. Use the periodicity of  $\langle y \rangle$  [see Eq.(17)] to write it as a Fourier series,

$$\sum_{m=1}^{\infty} \frac{(-1)^m}{\pi m} \sin(2\pi m y) = - \langle y \rangle \quad .$$

Integrate this repeatedly to evaluate

$$\sum_{m=1}^{\infty} \frac{(-1)^m}{(\pi m)^2} \cos(2\pi m y) , \quad \sum_{m=1}^{\infty} \frac{(-1)^m}{(\pi m)^3} \sin(2\pi m y) ,$$

$$\sum_{m=1}^{\infty} \frac{(-1)^m}{(\pi m)^4} \cos(2\pi m y) .$$

1-3. In order to establish Eq. (43), first use the one-dimensional statements

$$\frac{1}{2} p^2 - F x = e^{-i \frac{p^3}{6F}} (-F x) e^{i \frac{p^3}{6F}} ,$$

$$e^{-i F x t} p e^{i F x t} = p + F x t ,$$

which are illustrations of

$$e^{-i f(p)} x e^{i f(p)} = x - \frac{d}{dp} f(p)$$

and

$$e^{-i f(x)} p e^{i f(x)} = p + \frac{d}{dx} f(x) ,$$

to show that

$$e^{-i \left( \frac{1}{2} p^2 - F x \right) t} = e^{-i \frac{p^3}{6F}} e^{i F x t} e^{i \frac{p^3}{6F}}$$

$$= e^{i F x t} e^{-i \frac{1}{6F} (p + F t)^3} e^{i \frac{p^3}{6F}}$$

$$= e^{i F x t} e^{-i \frac{1}{2} \left( p + \frac{1}{2} F t \right)^2 t} e^{-i F^2 t^3 / 24} .$$

Generalize to three dimensions and arrive at Eq. (42).

1-4. The average value of  $r^2$  for an orbital state in the Bohr atom is

$$\langle r^2 \rangle_{m', l'} = \frac{m'^2}{2Z^2} [5m'^2 - 3l'(l' + 1)] ,$$

where  $m'$  is the principal quantum number and  $l' = 0, \dots, m' - 1$  the angular momentum quantum number. Average this over the  $l'$  values to find

$$\overline{(r^2)}_{m'} = \frac{m'^2}{4Z^2} (7m'^2 + 5) .$$

A measure for the size  $R$  of the atom is the average of  $r^2$ ,

$$N R^2 = \overline{(r^2)}_{\text{atom}} = \sum_{m'=1}^m 2m'^2 \overline{(r^2)}_{m'} + \mu 2(m+1)^2 \overline{(r^2)}_{m+1} .$$

Show that

$$R \cong \frac{\sqrt{3/4}}{Z} \left[ \left(\frac{3}{2}N\right)^{2/3} + \frac{1}{2} \right]$$

for large  $N$ . Compare with Eqs. (87) and (92).

1-5. The contribution of a full Bohr shell, with principal quantum number  $m'$ , to  $n_0$ , the electron density at the site of the nucleus, is given by

$$\frac{(2Z)^3}{4\pi} \left(\frac{1}{m'}\right)^3 .$$

Show that

$$n_0 = \frac{(2Z)^3}{4\pi} \left[ \sum_{m'=1}^{\infty} \left(\frac{1}{m'}\right)^3 - \frac{1}{2} \left(\frac{3}{2}N\right)^{-2/3} + O(N^{-4/3}) \right] ,$$

for a Bohr atom (without shielding) that contains  $N$  electrons.

1-6. Derive the identity

$$\sum_{m'=1}^m f(m') - \int_1^m dy f(y) = \int_1^m dy \left\langle y - \frac{1}{2} \right\rangle \frac{df(y)}{dy} + \frac{1}{2} [f(m) + f(1)]$$

(which, incidentally, was first proven by Euler) and use it to confirm Eq. (47).