A Note on Atomic Binding Energies*

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By the use of Dickinson's recent calculations of the diamagnetic field for atoms based on Hartree calculations, and a theorem due to Feynman, an expression is obtained for the total binding energy of the electrons in an atom as a function of atomic number. The results are compared with predictions of the Fermi-Thomas statistical model. It is found that the binding energy for small Z varies as $Z^{7/3}$ in accord with the statistical model but for high Z the dependence on Z becomes approximately $Z^{12/5}$. The equation for the binding energies is estimated to be correct to 5 percent or better.

THE Fermi-Thomas statistical model of the atom[1] is unique among atomic models in that, apart from a scale factor and normalization, it gives the same charge distribution to atoms of all atomic numbers. The linear dimensions of the charge distribution are fixed by an "atomic radius" a_Z which according to the theory varies with atomic number as $Z^{-4/3}$. The model then predicts that the total binding energy of an atom varies with atomic number as $Z/a_Z \sim Z^{7/3}$. There appears to be no experimental data which can be employed to check this Z-dependence for the heavier elements. It has been found,[2] however, that it is checked exceptionally well for the lighter elements (from helium to oxygen) in spite of the fact that the statistical model would be expected to be poor for such light elements.

An alternative method of checking this Z dependence of the total binding energy is to compare it with the results obtained on the basis of more accurate atomic models. The most natural choice of the latter is the Hartree model, and the comparison is greatly facilitated by recent calculations of Dickinson[3] of the internal diamagnetic field for atoms based on the results of Hartree calculations. Dickinson has presented a table of values for the electrostatic potential at the nucleus of an atom due to the electrons, computed from the Hartree electron distributions for all atoms for which Hartree calculations have been made. If one plots the logarithm of the electrostatic potential at the nucleus against the logarithm of the atomic number (Fig. 1), one finds that the points from He $(Z=2)$ to Hg $(Z=80$, the highest atomic number for which Hartree calculations are available) fall with remarkable precision $(\sim 1$ percent) on a straight line. The equation of the straight line[4] then gives the relation,

$$eV = (12/5)Z^{7/5}R, \qquad (1)$$

where e is the elementary unit of charge, V is the electrostatic potential, and R is the Rydberg in energy units $(R=13.595$ ev).

To relate eV as given by (1) with the total binding energy of an atom we make use of the following theorem due to Feynman:[5] *The partial derivative of an energy eigenvalue of a system with respect to a parameter occurring in its Hamiltonian is given by the expectation value of the partial derivative of the Hamiltonian operator with respect*
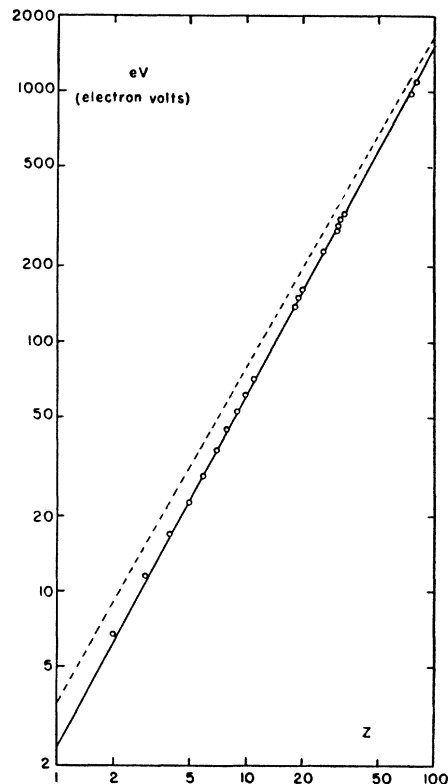

FIG. 1. Plot of logarithm of electrostatic potential at atomic nucleus due to electrons vs logarithm of atomic number from Hartree and Fermi-Thomas models. Circles represent values from Hartree model obtained by Dickinson. Dotted line represents result from Fermi-Thomas model. Full line is a plot of Eq. (1).

reasons: the convenient values obtained for the numerical coefficient and exponent and the fact that by this error we largely compensate the effects of a later approximation (see footnote 6).

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[1] See, for example, P. Gombas, *Die Statistische Theorie des Atoms und ihre Anwendung* (Springer-Verlag, Berlin, 1949); L. Brillouin, *L'Atome de Thomas-Fermi* (Hermann, Paris, 1934); E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, London, 1935), p. 336.

[2] G. Allard, J. phys. et radium 9, 225 (1948).

[3] W. C. Dickinson, Phys. Rev. 80, 563 (1950).

[4] It will be noted from Fig. 1 that the straight line represented by Eq. (1) is not the best straight line through the points but is slightly low for small Z. This choice has been made for two

[5] R. P. Feynman, Phys. Rev. 56, 340 (1939).

to the parameter. If we apply the theorem to an atomic system corresponding to a nucleus with charge Ze and Z' electrons, we find $(\partial E_B/\partial Z)=eV$, where E_B is the binding energy of the system, V is, as above, the electrostatic potential at the nucleus due to the electrons, and in the differentiation Z', the number of electrons, is held constant. If after the differentiation Z' is set equal to Z, then eV may be identified with the quantity in (1). Therefore, the difference in binding energies between an atom of atomic number $Z-1$ and the singly ionized atom of atomic number Z is given by[6]

$$\int_{Z-1}^{Z} eV(Z)dZ.$$

Hence the difference in binding energies between neutral atoms of atomic numbers $Z-1$ and Z is given by

$$E_B(Z)-E_B(Z-1)=\int_{Z-1}^{Z} eV(Z)dZ+I_Z, \qquad (2)$$

where I_Z is the first ionization potential of the atom of atomic number Z. From (2) one obtains easily by summation and the use of (1):

$$E_B(Z)=\int_{2}^{Z} eV(Z)dZ+ \sum_{z=3}^{Z} I_z+E_B(2)$$

$$=Z^{12/5}R+ \sum_{z=2}^{Z} I_z-1.278R, \qquad (3)$$

TABLE I. Calculated and experimental atomic binding energies in electron volts.

Z	E_B Hartree [Eq. (3)]	E_B Fermi-Thomas [Eq. (4)]	E_B Modified Fermi-Thomas [Eq. (5)]	E_B* [Exp.]
2	78.63	105.0	79.40	78.63
3	202.1	270.1	204.2	202.49
4	400.3	529.0	399.5	397.15
5	676.8	890.5	672.5	667.59
6	1041	1363	1029	1024.87
7	1506	1952	1474	1473.37
8	2068	2666	2013	2032.98
10	3535	4486	3388	
20	1.833×10^4	2.262×10^4	1.708×10^4	
30	4.811×10^4	5.824×10^4	4.398×10^4	
40	9.590×10^4	1.140×10^5	8.607×10^4	
50	1.637×10^5	1.918×10^5	1.449×10^5	
60	2.532×10^5	2.934×10^5	2.216×10^5	
70	3.663×10^5	4.207×10^5	3.177×10^5	
80	5.049×10^5	5.744×10^5	4.338×10^5	
90	6.705×10^5	7.561×10^5	5.710×10^5	

* From tabulation in reference 2.

[6] It will be noted that this expression is not quite correct, since Eq. (1) considered as an interpolation formula between integral values of Z corresponds to the charge on the electrons being kept equal to the charge on the nucleus as the atomic number varies from $Z-1$ to Z. An estimate of the error committed can be obtained by comparing the value of eV for a neutral atom and for the atom with one electron removed. Dickinson's table includes values for ions where the Hartree calculations are available, and from these it is found that the error in the integrand is largely compensated for all Z by the error in Eq. (1) discussed in footnote 4.

where the binding energy of He has been used as the base from which the summation is extended. Since the first ionization potentials for practically all the elements are known, $E_B(Z)$ can immediately be calculated with the results tabulated in Table I. Also tabulated are the results obtained from the Fermi-Thomas statistical model:

$$E_B(Z)=20.83Z^{7/3} \text{ ev}, \qquad (4)$$

and from another expression of the same form:

$$E_B(Z)=15.73Z^{7/3} \text{ ev}, \qquad (5)$$

but with the coefficient adjusted[2] to give better agreement with the known binding energies of the light atoms. It will be noted from the table that the binding energy apparently increases more rapidly with Z than the $Z^{7/3}$ relation given by the Fermi-Thomas model, and for large Z is more closely represented by a $Z^{12/5}$ dependence. While (3) is not quite as accurate as (5) in representing the experimental binding energies of the light atoms (see Table I), it would appear that the good agreement with (5) is at least partly fortuitious.

The fact that the Z-dependence of binding energy as given by the Fermi-Thomas model does not approach asymptotically the result from the Hartree calculations (assuming the latter to be more correct) for asymptotically large Z might be considered puzzling, in view of the common statement that the Fermi-Thomas model should give essentially correct results for large Z where the statistical assumptions should be well satisfied. As a possible reason for this discrepancy we might point to the fact that the electronic charge distribution predicted by the Fermi-Thomas model is always incorrect in the neighborhood of the nucleus, regardless of how large Z may be, because of the singularity in the coulomb field at the nucleus. The $1/r$ singularity in the coulomb potential due to the nucleus results in an electronic charge density which varies as $r^{-\frac{1}{2}}$ in the neighborhood of the nucleus, while actually the electronic charge density should be constant in this neighborhood. This "pulling in" of electronic charge in the neighborhood of the nucleus affects the binding energy of the atom in two ways. First, it increases the binding energy because of the larger potential energy of interaction between this charge and the nuclear charge. Secondly, it more effectively shields the outer parts of the electronic charge distribution from the nuclear charge resulting in a "pulling away" of these outer parts of the charge distribution from the nucleus. This results in a decrease in their potential interaction with the nucleus and a decrease in the total binding energy. If the first of these effects is dominant, we would have at least a qualitative explanation of the high Fermi-Thomas binding energy relative to that obtained from the Hartree model.

Our conclusions may be summarized as follows:

(1) On the basis of Hartree calculations one finds that the total binding energy of atoms as a function of

atomic number varies approximately as $Z^{4/3}$ (in agreement with the predictions of the Fermi-Thomas statistical model of the atom, but with a different proportionality constant) for the light atoms, but the binding energy varies as $Z^{12/5}$ for heavy atoms. Consequently, binding energies for atoms near the end of the periodic table will be approximately 15 percent too low when calculated by the Fermi-Thomas expression with a coefficient chosen to give agreement with experimental values for the light elements.

(2) In so far as the charge distribution in heavy atoms can be specified by a single "atomic radius," this atomic radius varies with Z approximately as $Z^{-7/5}$.

(3) On the basis of Dickinson's estimates of the accuracy of the values of eV given by (1), one would estimate that the accuracy of Eq. (3) for atomic binding energies should be 5 percent or better.

Unfortunately, the possibility of a direct experiment test of the foregoing conclusions appears very remote at the present time.

The Theory of Internal Conversion*

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The theory of the internal conversion process is presented on a firm quantum-mechanical foundation and in a form most convenient for calculations. The question of the correct gauge for the radiation potentials and the effect of the finite size of the nucleus on these potentials are considered.

I. INTRODUCTION

THE theory of the internal conversion process has been developed by Mott[1] and by Taylor and Mott[2] on the basis of correspondence principle arguments. In 1936, Hulme[3] discussed the interaction of two particles in a form applicable to the theory of internal conversion. This paper put the theory on a firm quantum-mechanical foundation so far as the matrix elements used in the calculation of N_e, the number of electrons ejected per second, were involved. Unfortunately, Hulme's explicit introduction of the coulomb direct interaction and his expansion of the radiation field in a series of plane rather than spherical waves made it impossible to compare the theory directly with the prescription followed by the calculators of internal conversion coefficients. Up to the present date, no rigorous quantum-mechanical derivation of the matrix elements used in the calculation of N_q, the number of gamma-quanta emitted per second, has been presented.

In view of the recent exact calculations of internal conversion coefficients,[4-6] it seems that a rigorous quantum-mechanical investigation of the internal conversion process is desirable.

II. THE PROBLEM

It is desired to calculate the transition probability from the initial state in which the nucleus is excited, the electron is in its ground state (bound electron), and no quanta are present to a final state in which the nucleus is in its ground state, the electron is in its excited state (continuum electron), and no quanta are present. The nucleus and the electron interact with each other only through the electromagnetic field coupling. Since no quanta are present initially or finally, the intermediate states are those for which a single quantum is present, and either both nucleus and electron are in their ground states (first intermediate state) or both are excited (second intermediate state). The first intermediate state corresponds to a double process in which the nucleus makes a transition to its ground state and emits a gamma-quantum, and the electron makes a transition to its excited state and absorbs this quantum. Since the intermediate state need not conserve energy, the energy of the gamma-quantum does not have to equal the initial excitation energy of the nucleus. The second intermediate state corresponds to a double process in which the electron makes a transition to its excited state and emits a gamma-quantum, and the nucleus makes a transition to its ground state and absorbs this quantum. In this case it is apparent that the intermediate state cannot conserve energy.

The description of the states is summarized in Table I.

* Part of a dissertation submitted by one of us (N.T.) in partial fulfillment of the requirements for the Ph.D. degree at New York University.
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[1] N. F. Mott, Ann. inst. Henri Poincaré 4, 207 (1933).
[2] H. M. Taylor and N. F. Mott, Proc. Roy. Soc. (London) A142, 215 (1933).
[3] H. R. Hulme, Proc. Roy. Soc. (London) A154, 487 (1926).
[4] Rose, Goertzel, Spinrad, Harr, and Strong, Phys. Rev. 76, 1883 (1949); and privately circulated tables of results.
[5] B. A. Griffith and J. P. Stanley, Phys. Rev. 75, 534 (1949).
[6] J. R. Reitz, Phys. Rev. 77, 10 (1950).