The Effect of Exchange and Correlation on Binding Energy of Compressed Atoms

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(Received June 25, 1960)
(Revised Manuscript Received February 3, 1961)

In the binding energy formula the effect of exchange has been taken by making use of the T. F. D. function. Correlation has been incorporated as a perturbation and the effect of finite boundary has been taken as given by Scott. The agreement between the calculated values and the experimentally observed ones is much better than provided by Scott.

Introduction

The Thomas-Fermi statistical model of an atom has been used by various investigators in their pursuit to study the properties of solids and of atoms which however should be reasonably independent of the electron shell structure. The model has been used for approximate calculations of potential fields and the charge densities inside an atom, thereby leading to the calculation of equation of state, binding energy, etc., of various atoms. Milne (1927) suggested a formula $20.92 Z^{15/2}$ ev representing the variation of binding energy with respect to $Z$. This formula, however, gives values of binding energy of atoms which are some 20 to 30 percent higher than the experimentally observed ones, derived from spectroscopic analysis. The binding energy was found to be smoothly varying as $Z^{12/3}$ for high values of $Z$ and as $Z^{11/3}$ for low $Z$ with different coefficients.

Scott (1952) suggested that the effect of finite boundary and that of exchange have to be incorporated and he gave that the corrections are $-13.6 Z^2$ and $6.01 Z^{13/3}$ ev respectively. However, it appears that though the agreement between the theoretical values and those observed experimentally is better, some discrepancy has yet to be accounted for.

The purpose of the present paper is to make an attempt in the direction of accounting for the discrepancy still left. In the above derivations the correlation energy of electrons has not been taken into account. We shall incorporate the correlation energy in the analysis and calculate its contribution to the binding energy of an atom. We make use of the potential distribution inside an atom as given by Feynman, Metropolis and Teller (1949) and regard the correlation energy as perturbation to calculate its effect on the binding energy of an atom.
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I

Binding energy of an atom can be related with the potential distribution inside the atom by making use of Feynman's theorem:

"The partial derivative of an energy eigenvalue of a system with respect to a parameter occurring in the Hamiltonian is given by the expectation value of the partial derivative of Hamiltonian operator with respect to the parameter."

\[ \langle \frac{\partial H}{\partial Z} \rangle = -V, \]  

(1)

where \( V \) is the potential at the nucleus due to the charge distribution of the electrons,

\[ -V = \lim_{r \to 0} \frac{Ze}{r} (1 - \zeta) \]

(2)

\[ = -\frac{ze}{\mu} \zeta'(0), \]

where \( \zeta(r) \) represents the electrostatic potential at a distance \( r \) from the nucleus as a fraction of the potential due to the nucleus itself and \( \mu \) is a scale factor:

\[ r = \mu x \quad \mu = \left( \frac{9\pi^2}{128Z} \right)^{1/3} a_0 = 0.88534 a_0 Z^{-1/3}. \]

(3)

Milne,\(^5\) while calculating the binding energy of an atom, made use of Baker's\(^6\) constant \( \zeta'(0) = -1.5881 \) based on the Thomas-Fermi model of an atom. This leads to the well-known formula,

\[ V = -48.80 Z^{4/3} \]

(4)

which gives for the binding energy \( W \) the expression

\[ W = 20.92 Z^{7/3} \text{ ev.} \]

(5)

In the foregoing the atom is considered to be free with its boundary extending to infinity, and the binding energy formula has to be corrected in the light of a finite boundary of the atom. Scott\(^7\) (1952) has effectively estimated the correction to be applied to the T.F. formula by comparing the results of T.F. approximation with exact wave mechanical treatment for the case of particles moving in a Coulomb field. He gave the correction as \(-13.6 Z^2 \text{ ev.}\)

He also modified Milne's formula by taking the effect of exchange energy of electrons by regarding exchange simply as perturbation and taking T.F. density distribution. According to him the contribution of exchange to the binding energy is
\[
\frac{4\mu Z^2}{\pi^3} \int_0^\infty x^2 \, dx, \quad \int_0^\infty x^4 \, dx = 0.616. \tag{6}
\]

Thus

\[
W = 20.92 Z^{7/3} - 13.6 Z + 6.01 Z^{3/2} \text{ ev.} \tag{7}
\]

II

Dirac\(^7\) (1930) introduced exchange into the Thomas-Fermi theory and arrived at the differential equation for potential distribution

\[
\frac{d^2 \psi}{dx^2} = x \left( \epsilon + \frac{\psi^{1/3}}{x^{1/3}} \right)^3. \tag{8}
\]

\(x\) has the same meaning as in I and

\[
\epsilon = \left( \frac{3}{32} \pi^3 \right)^{1/3} Z^{-2/3} = 0.21178 Z^{-2/3}. \tag{9}
\]

The potential without exchange effect, denoted by \(-V_0\), is connected with \(\psi\) by the relation

\[
-eV_0 = E_0 + \frac{2me^4}{\hbar^2} - \frac{Ze^2 \psi}{\mu x}. \tag{10}
\]

The foregoing equations have been obtained by including exchange energy term in the expression for the energy of an electron. The electron density is now connected to the electro-static potential energy by the relation

\[
n = \frac{8\pi}{3\hbar^3} \left[ \frac{2me^2}{\hbar} + \left\{ \frac{4m^2e^4}{\hbar^2} + 2m(E + eV_0) \right\}^{1/3} \right]. \tag{11}
\]

Feynman, Metropolis and Teller\(^5\) (1949) have solved the above equations numerically for the potential distribution inside an atom for carbon and uranium at absolute zero temperature. They have arrived at the result for carbon at normal density,

\[
\psi'(0) = -1.686 \quad \text{and} \quad x_0 = 6.28.
\]

According to Feynman's theorem the T.F.D. equation leads to

\[
-V = -\frac{\psi_x'(0)}{\mu} \frac{Ze}{\mu}. \tag{12}
\]

But the exact definition of \(\psi(x)\) gives

\[
-V = 3.4 \frac{Ze}{\mu} \psi_x'(0)
\]

instead of the above equation, where 3.4 is nothing but \(1/16 \epsilon_0^2\) in Gombás\(^9\) notation. Thus
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\[ W = -13.17 \psi_x'(0) Z^{13} - 13.6 Z^2 + 3.4 Z, \quad (13) \]

where the boundary effect has also been included. For carbon one arrives at \( W = 993.3 \text{ ev} \), and for other atoms one has simply to put the corresponding value of \( \psi_x'(0) \). Slater and Krutter\(^9\) have solved the T.F.D. equation for \( Z = 3, 11 \) and 29 and Jensen\(^10\) for \( Z = 18, 36 \) and 54.

### III

We shall now calculate the contribution of correlations to the binding energy of an atom.

Wigner\(^11\) has calculated the correlation per electron as \(-0.89 e^2/r_s\), which is equal to the difference between the exact solution of Hartree Fock’s equations and the exact solution of the problem; \( r_s \) is given by \( n^{-1} = 4\pi/3 \cdot r_s^3 \). Wigner’s result, however, is correct only in the low density limit \((r_s \geq 20)\). Lately Gell-Mann and Brueckner\(^12\) (1957) have derived an expression for the average correlation energy per electron by writing down the important part of the perturbation expansion for the energy when the electrons are in Coulomb interaction with each other and adding both over all the electrons and perturbation series. They have arrived at the expression true for high density limit \((r_s \leq 1)\)

\[ \varepsilon_{\text{corr}} = -\left( \frac{me^4}{\pi^2 \hbar^2} \right) (1 - \ln 2) \ln P + \text{constant}, \quad (14) \]

where \( P \) is the momentum at the top of Fermi distribution of the degenerate electron gas. Lewis\(^13\) (1958) has taken account of both the above results in an interpolation formula

\[ \varepsilon_{\text{corr}} = -\left( \frac{me^4}{\pi^2 \hbar^2} \right) (1 - \ln 2) \ln \left[ 1 + \frac{(0.89 \alpha - 1)}{(1 - \ln 2) \hbar} \pi P a_0 \right], \quad (15) \]

where \( \alpha = (4/9\pi)^{1/3} \) and the above can be put in terms of \( r_s \) as

\[ \varepsilon_{\text{corr}} = -0.8464 \ln \left[ 1 + \frac{0.897}{r_s} \right]. \]

When the correlation energy is incorporated into the T.F.D. equation, the equation becomes quite cumbersome and a solution can be obtained with a great pain but without much benefit for our purpose. Lewis\(^13\) has tried to take account of correlation energy and has given a differential equation but no numerical results have so far been reported. We may, however, use the density distribution given by the unmodified T.F.D. equation and regard correlation merely as a perturbation, and calculate the contribution of correlation to the binding energy of an atom.

In the following we shall make use of a more suitable formula given by Pines\(^14\) (1955) for the region of actual metallic densities \((r_s = 1.8 \) to 5.6\). He has given the result as
using the plasma-oscillation picture based on the collective description of electron interactions due to Bohm and Pines\(^{(14)}\) (1952). The contribution of correlations to the binding energy can be written in the form

\[
W_{c} = -\int n \varepsilon_{corr} \, dv
\]

\[
= 4\pi \int n f(n) r^3 \, dr,
\]

where

\[
f(n) = 1.768 + 0.142 \ln n \text{ ev.}(18)
\]

T.F.D. analysis gives the electron density as expressed in Eq. (11). On combining the two equations (10) and (11) we get

\[
n(x) = \frac{8\pi}{3h^3} \left[ \frac{2me^2}{\hbar} + \left( \frac{2mZe^2\phi}{\mu x} \right)^{1/3} \right] = a[1 + bZ^{2/3}(\phi/x)^{1/3}],
\]

where

\[
a = \frac{1}{3\pi^5} a_0^3
\]

and

\[
b = 4.722.
\]

Substituting the above expression of \(n\) into the expression (17),

\[
W_{c} = 4\pi \rho^2 a \int_{0}^{a_0} \left[ F(x) \right]^3 [1.768 + 0.142 \ln (aF^3)] x^2 dx,
\]

\[
F(x) = 1 + bZ^{2/3}(\phi/x)^{1/3}.
\]

The above integral has to be evaluated numerically and for this purpose Chebyshev integration formula is very useful. According to Chebyshev\(^{(16)}\)

\[
\int_{y_{1}}^{y_{2}} g(y) \, dy = \frac{y_{2} - y_{1}}{N} \sum_{r=1}^{N} g(y_{r}),
\]

where

\[
y_{r} = \frac{y_{2} + y_{1}}{2} + \frac{y_{2} - y_{1}}{2} \alpha_{r},
\]

\(\alpha_{r}\) is independent of \(g(y)\) and depends solely on \(N\). In the present calculations \(N\) has been chosen equal to 6 and for this \(N\), \(\alpha_{r}\)'s are ±0.26665, ±0.42252 and ±0.86625.

The numerical results obtained by method are shown in Table I. The Table I tells us that the agreement between the binding energy calculated by the author and that experimentally observed is better than that provided by Scott. Mention may also be made of Tomishima’s result of correlation
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Table I.

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>$-\phi'_z(0)$</th>
<th>$W_e$</th>
<th>$W$ Correlation included</th>
<th>$W_{cap}$</th>
<th>$W$ Scott formula</th>
</tr>
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<tr>
<td>carbon</td>
<td>6</td>
<td>1.686</td>
<td>2.0</td>
<td>37.8</td>
<td>37.8</td>
<td>36.7</td>
</tr>
<tr>
<td>argon</td>
<td>18</td>
<td>1.635</td>
<td>9.5</td>
<td>522.5</td>
<td>528</td>
<td>518</td>
</tr>
<tr>
<td>krypton</td>
<td>36</td>
<td>1.6175</td>
<td>11.5</td>
<td>2718.8</td>
<td></td>
<td></td>
</tr>
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</table>

In the Table atomic units are used.
* This result is given by Tomishima.\(^{17}\)

energy of krypton which seems to be less plausible than the one calculated by the method used in this paper.

It is however to be noted that the above analysis suggests that the binding energy is a function of density (and that of temperature) since the value of $\phi'_z(0)$ depends upon density (and on temperature) under consideration, as is shown in Table II.

Table II. Variation of binding energy with density at zero degree absolute.

<table>
<thead>
<tr>
<th></th>
<th>$x_0$</th>
<th>$\rho$ gm/cc</th>
<th>Binding energy</th>
</tr>
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<tbody>
<tr>
<td>carbon</td>
<td>1.6740</td>
<td>3.262</td>
<td>8.35</td>
</tr>
<tr>
<td>carbon</td>
<td>1.6800</td>
<td>3.715</td>
<td>5.65</td>
</tr>
<tr>
<td>carbon</td>
<td>1.6840</td>
<td>4.378</td>
<td>3.45</td>
</tr>
<tr>
<td>carbon</td>
<td>1.6868</td>
<td>5.168</td>
<td>2.10</td>
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<tr>
<td>carbon</td>
<td>1.6863</td>
<td>5.729</td>
<td>1.54</td>
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<tr>
<td>carbon</td>
<td>1.6867</td>
<td>7.008</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Energy is given in atomic units.

It is seen from the above Table that as the density decreases the binding energy increases and appears to tend to a particular limit.

Acknowledgements

The author’s grateful thanks are due to Professor D.S. Kothari and Professor F.C. Auluck for their interest and encouragement throughout the present investigation.

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