A REFINEMENT OF THE THOMAS-FERMI MODEL AT SMALL DISTANCES

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Submitted to JETP editor November 29, 1958; resubmitted January 7, 1959

J. Exptl. Theoret. Phys. (U.S.S.R.) **36**, 1533-1535 (May, 1959)

A correction to the Thomas-Fermi model at small distances from the nucleus is suggested; this leads to a significant improvement in the agreement between the calculated and experimental values of the total energy of atoms.

IT is well known that the Thomas-Fermi model corresponds to the quasi-classical approximation to the Hartree equation. The Hartree equation has the following symbolical form in operator form:[1]

$$\nabla^2 B = -e\rho_{\text{nucl}} + \frac{8\pi e}{(2\pi\hbar)^3}\int \rho(\hat{H})\, d^3p, \qquad (1)$$

where ρ_{nucl} is the nuclear charge density ($\sim Z\delta(\mathbf{r})$), $\rho(\hat{H})$ the occupation-number operator for electrons of the form

$$\rho(\hat{H}) = (1 + \exp\{(\hat{H} - \mu)\beta\})^{-1}. \qquad (2)$$

Here $\beta = 1/kT$, T: temperature, $\hat{H}$ the Hamiltonian operator in the self-consistent approximation:

$$\hat{H} = (\mathbf{p} - i\hbar\nabla)^2/2m - eB(\mathbf{r}). \qquad (3)$$

In the quasi-classical approximation one can neglect $i\hbar\nabla$ and Eq. (1) is the same as the Thomas-Fermi equation. We get the quantum correction to the Thomas-Fermi model if we expand (2) in a power power series in $i\hbar\nabla$ acting upon $B(\mathbf{r})$. It is then essential that in the quasi-classical approximation the lower limit of the energy spectrum of $\hat{H}$ is equal to $-\infty$ which leads to an incorrect value for the density matrix (and all other quantities) at small distances from the nucleus. Using perturbation theory to take the quantum corrections approximately into account does not alter the position in this respect because the lower limit of the energy spectrum is essentially determined by all quantum corrections. However, the lower bound of the energy spectrum for atomic levels does not lie below the lowest level of a hydrogen-like atom with charge Z. This is a simple consequence of the screening influence of the atomic electrons and is confirmed experimentally. It is thus natural to attempt to generalize the occupation number operator, while not changing it in the strict sense, in such a way that also in the quasi-classical approximation the lowest level of $\hat{H}$ is bounded, and thus without violating the basic properties of the system (for instance, the virial theorem and the thermodynamic relations). This can be achieved if we propose instead of (2) for $\rho(\hat{H})$ the following expression:

$$\rho(\hat{H}) = \theta_+(\hat{H} - \mu - E_{min})(1 + \exp\{(\hat{H} - \mu)\beta\})^{-1}, \qquad (4)$$

where $\theta_+(x) = 1$ when $x > 0$, and $\theta_+(x) = 0$ when $x < 0$;

$$E_{min} \approx -e^4 m Z^2 b/2\hbar^2, \qquad 1 \leqslant b \leqslant 2.$$

If all quantum corrections are taken into account ($\hat{H} - \mu$) > E_{min} and expression (4) is equivalent to Eq. (2). At the same time, when the quantum corrections are taken into account approximately or in the quasi-classical approximation expression (4) leads to a more correct distribution for B and determines the thermodynamic characteristics of the atomic system more accurately.

Using (1) to (4) in the quasi-classical approximation we get a generalized Thomas-Fermi model. It is then expedient to go over to new variables and to introduce the following notation:

$$x = r/r_0; \qquad \varphi(x)/x = (\mu + eB)\beta, \qquad (5)$$

where r_0 is the radius of the atom and where we have introduced the notation

$$I_n(\eta, \alpha(\eta)) = \int_{\alpha(\eta)}^{\infty} y^n [1 + \exp(y - \eta)]^{-1} dy, \qquad (6)$$

$$\alpha(\eta) = (\eta - |E_{min}|\beta)\theta_+(\eta - |E_{min}|\beta). \qquad (7)$$

Using (5) to (7) we get from (1) to (4) the following equation for $\varphi(x)$ in the quasi-classical approximation:*

*In the practically most interesting case $|E_{\text{min}}|\beta \gg 1$ we have

$$I_n(\eta, \alpha(\eta)) = \begin{cases} [\eta^{n+1} - (\eta - |E_{min}|\beta)^{n+1}]/(n+1) & \text{if } \eta \geqslant |E_{min}|\beta \\ I_n(\eta, 0) & \text{if } \eta \leqslant |E_{min}|\beta. \end{cases}$$

$$\varphi''(x) = axI_{1/2}\left(\frac{\varphi(x)}{x},\ \alpha\left(\frac{\varphi(x)}{x}\right)\right) \tag{8}$$

with the boundary conditions

$$\varphi'(1) = \varphi(1), \qquad \varphi(0) = Ze^2\beta/r_0, \tag{9}$$

where

$$a = (r_0/c)^2, \qquad 1/c = 4\pi e(2m)^{3/4}/(2\pi\hbar)^{3/2}\beta^{1/4}. \tag{10}$$

The thermodynamic characteristics of the system (pressure p, average energy E) are expressed in terms of $\varphi(x)$ as follows:*

$$pV = \frac{2}{9}ZkT\,\frac{a}{\varphi(0)}I_{3/2}(\varphi(1),\ 0),$$

$$E = E_{kin} + E_{pot},$$

$$E_{pot} = -\frac{ZkTa}{2\varphi(0)}\int_0^1 x[\varphi(x) - \varphi(1)x + \varphi(0)]$$

$$\times I_{1/2}\left(\frac{\varphi(x)}{x},\ \alpha\left(\frac{\varphi(x)}{x}\right)\right)dx,$$

$$E_{kin} = \frac{ZkTa}{\varphi(0)}\int_0^1 x^2 I_{3/2}\left(\frac{\varphi(x)}{x},\ \alpha\left(\frac{\varphi(x)}{x}\right)\right)dx. \tag{11}$$

The virial theorem has the usual form

$$2E_{kin} + E_{pot} = 3pV,$$

V: atomic volume. In particular, we get for T = 0 from (8) (see reference 2 for the notation):

$$x^{1/2}d^2\chi/dx^2 = \chi^{3/2} - (\chi - \lambda x)^{3/2} \quad \text{when } x \leqslant \chi/\lambda,$$
$$x^{1/2}d^2\chi/dx^2 = \chi^{3/2} \quad \text{when } x \geqslant \chi/\lambda, \tag{12}$$

where

$$\lambda = 0.885\,|\,E_{min}\,|\,Z^{-4/3}. \tag{13}$$

Here $\chi(0) = 1$. The further discussion is given for the case of an isolated atom and the boundary condition is therefore of the form: $\chi'(\infty) = 0$.

As we indicated already, the quantity E_{min} must be not more than the lowest energy of a hydrogen-like atom. According to (13) we have thus $\lambda \geq 0.45\,Z^{2/3}$. If we take for λ its limiting value $\lambda = 0.45\,Z^{2/3}$; we get, solving Eq. (12), for the total energy (E) of an atom the value

$$E_{av} \approx 15.9Z^{7/3}\ \text{ev} \quad \text{for } 50 \leqslant Z \leqslant 90,$$

which agrees appreciably better with experimental values than in the case of the usual Thomas-Fermi model (in the usual Thomas-Fermi model[2] $E = 20.94\,Z^{7/3}$ ev). We obtain an even better agreement with the experimental values for E, if we use for λ $\lambda = 0.9\,Z^{2/3}$ (which corresponds to $|E_{min}|$ equal to twice the energy of the lowest level of the hydrogen-like atom). This means that for such a choice of λ all quantum and exchange corrections to the generalized Thomas-Fermi model are minimum.

In the table we give the calculated values of E in the case where $\lambda = 0.9\,Z^{2/3}$.

Z	$E_{calc}\,Z^{-7/3}$ ev	$(E_{exp} - E_{calc})/E_{exp}$
26	15.9	0.06
36	16.2	0.053
54	16.7	0.047
80	16.9	0.05
92	17.1	0.056

We must note that a method of cutting off the energy can be applied successfully also to other problems in statistical or nuclear physics. The advantage of this method compared with cut-offs in x- or p-space lies in the fact that it corresponds to a formfactor which commutes with the total Hamiltonian and which thus does not violate the general properties of the system.

The author thanks D. A. Kirzhnits for useful discussions and L. V. Pariiskiĭ for carrying out the numerical calculations.

*In deriving (11) we have used the relation

$$\frac{d}{dx}I_n(\eta(x),\ \alpha(\eta(x))) = n\,\frac{d\eta(x)}{dx}\,I_{n-1}(\eta,\ \alpha(\eta)).$$

[1] D. A. Kirznits, J. Exptl. Theoret. Phys. (U.S.S.R.) **32**, 115 (1957), Soviet Phys. JETP **5**, 64 (1957).

[2] L. D. Landau and E. M. Lifshitz, Квантовая механика (Quantum Mechanics) Gostekhizdat, p. 270, 1948, Quantum Mechanics, Pergamon Press, London, 1958.

Translated by D. ter Haar
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