Acta Physica Academiae Scientiarum Hungaricae, Tomus 27, pp. 441—448 (1969)

NEW FOUNDATIONS FOR THE THOMAS–FERMI MODEL*

By

R. GÁSPÁR

INSTITUTE OF THEORETICAL PHYSICS, KOSSUTH LAJOS UNIVERSITY, DEBRECEN 10

and

RESEARCH GROUP FOR THEORETICAL PHYSICS, HUNGARIAN ACADEMY OF SCIENCES, BUDAPEST

(Received 20. II. 1969)

It is demonstrated that the atomic model, in which the zero order approximations to the one electron orbitals are hydrogen like orbitals, always leads to a model which imitates very closely the Thomas—Fermi model of the statistical theory of the atoms.

The Schrödinger equation and zero order solutions

For an atom with atomic number Z the Hamiltonian has the form [1]

$$\begin{aligned}\mathbf{H} &= -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\Delta_i - Z\sum_{i=1}^{Z}\frac{e^2}{r_i} + \sum_{j>i=1}^{Z}\frac{e^2}{r_{ij}} = \\ &= Z^2\left\{-\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\Delta_{\varrho_i} - \sum_{i=1}^{Z}\frac{e^2}{\varrho_i} + \frac{1}{Z}\sum_{j>i=1}^{Z}\frac{e^2}{\varrho_{ij}}\right\} = Z^2\,\mathbf{H}_\varrho\,,\end{aligned} \tag{1}$$

where we have introduced the scaled coordinates with the relation [1]

$$\varrho = \mathbf{r}Z\,. \tag{2}$$

The Schrödinger equation

$$\mathbf{H}\Psi = E\Psi \tag{3}$$

has perturbation solution with the energy

$$\frac{E}{Z^2} = W_2 + W_1\frac{1}{Z} + W_0\frac{1}{Z^2} + 0\left(\frac{1}{Z^3}\right) \tag{4}$$

in which

$$W_2 = -\frac{1}{2}\sum_{\alpha=1}^{k} q_\alpha\frac{1}{n_\alpha^2}\frac{e^2}{a_0} \tag{5}$$

* Dedicated to Prof. P. GOMBÁS on his 60th birthday.

is the sum of the hydrogenic energy terms. a_0 is the first Bohr radius in the hydrogen atom and e^2/a_0 is the atomic unit of the energy 27.23 eV; q_α is the occupation number of the states, with principal quantum number n_α. W_1 is determined by the electrostatic interaction matrix. For closed shells the occupation numbers are

$$q_\alpha = 2\, n_\alpha^2 \tag{6}$$

and the total number of electrons is

$$Z = \sum_{\alpha=1}^{k} q_\alpha = 2 \sum_{\alpha=1}^{k} n_\alpha^2 = 2\, \frac{k\,(k+1)\,(2k+1)}{6} = \frac{2}{3}\left(k+\frac{1}{2}\right)^3 - \frac{1}{6}\,k - \frac{1}{12}, \tag{7}$$

so that approximately

$$k = -\frac{1}{2} + \left(\frac{3}{2}\right)^{1/3} Z^{1/3}. \tag{8}$$

By inserting (6) and (8) into (5) we get

$$W_2 = \frac{1}{2} - \left(\frac{3}{2}\right)^{1/3} Z^{1/3} \tag{9}$$

which is the zeroth order approximation to E/Z^2. By investigating the case for non closed shells it turns out that equation (9) represents W_2 for non closed shells to a good approximation also.

Energy theorems

Because of the Coulomb forces in the Hamiltonian (1) the virial theorem

$$E = -E_k = \frac{1}{2}\,(E_p^n + E_p^e) \tag{10}$$

is valid, where we have introduced the kinetic energy E_k, the electron—nucleus interaction energy E_p^n and the electron—electron interaction energy E_p^e which add up to the total energy

$$E = E_k + E_p^n + E_p^e \tag{11}$$

with the explicit expressions as follows

$$E_p^n = -Ze^2 \int \frac{\varrho(\mathbf{r})}{r}\, dv\,, \tag{12}$$

$$E_k = -\frac{\hbar^2}{2m} \sum_{i=1}^{Z} \langle \Psi | \Delta_i | \Psi \rangle\,, \tag{13}$$

$$E_p^e = \frac{1}{2}\, e^2 \int \frac{\varrho(\mathbf{r})\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, dv\, dv'. \tag{14}$$

In a previous paper [2] we have made use of the Hellmann–Feynman theorem stating

$$\frac{\partial E}{\partial Z} = \frac{1}{Z} E_p^n \tag{15}$$

and a combination of this theorem with the virial theorem gave us for neutral atoms

$$\frac{E_p^e}{E} = - Z \frac{d}{dZ} \left\{ \log \left(\frac{-E}{Z^2} \right) \right\}_{N=Z} . \tag{16}$$

By introducing $-W_2$ i.e. the zeroth order approximation for $-E/Z^2$ we get after some manipulation

$$\frac{E_p^e}{E} = - \frac{1}{3} - \frac{1}{6 \left(\frac{3}{2} \right)^{1/3}} \frac{1}{Z^{4/3}} . \tag{17}$$

The second term in (17) is negligible for greater atomic numbers and we may use

$$\frac{E_p^e}{E} = - \frac{1}{3} \tag{18}$$

as a first approximation. (18) shows us that dependence of E_p^e and E and consequently that of E_p^n on the atomic number is expressed by the same power of Z which determines the logarithmic derivative and so the ratio E_p^e/E. Therefore the equation $E_p^e/E = -1/3$ is true with a much higher accuracy. Using the virial theorem, it is easy to demonstrate that this is equivalent to

$$\frac{E_p^n}{E_p^e} = - 7 \tag{19}$$

which is a well known theorem of the Thomas–Fermi theory [3].

We are going to make use of relations (18) and (19). By the aid of a scale transformation we get the following relation

$$E(\lambda) = \lambda^2 E_k^0 + \lambda E_p^{n0} + \lambda E_p^{e0} \tag{20}$$

and for the minimum value

$$\lambda_0 = - \frac{E_p^{n0} + E_p^{e0}}{2 E_k^0} \tag{21}$$

and

$$E(\lambda_0) = - \lambda_0^2 E_k^0 . \tag{22}$$

The zeroth order values are

$$E_k^0 = -W_2\,, \tag{23}$$

$$E_p^{n0} = 2W_2 = -2E_k^0 \tag{24}$$

and

$$E_p^{e0} = -\frac{1}{7} E_p^{n0}. \tag{25}$$

As a consequence

$$\lambda_0 = \frac{6}{7}$$

and

$$E(\lambda_0) = \left(\frac{6}{7}\right)^2 W_2 = \frac{18}{49} Z^2 - \frac{36}{49}\left(\frac{3}{2}\right)^{1/3} Z^{7/3}, \tag{26a}$$

or because the first term is much smaller than the second we get by an averaging process

$$E(\lambda_0)_a = -0.712\,866\, Z^{7/3}. \tag{26b}$$

Scaling and invariance

In this Section we investigate the consequences of the above results. We introduce a scaling of the coordinates and the charge density by the following relations

$$\mathbf{r} = Z^a \mathbf{r}' \quad \text{and} \quad \varrho = Z^b \varrho'. \tag{27}$$

The primed quantities in the above and following equations denote scaled quantities.

Equations (27) lead us to a scaling of the energy and the normalization condition in the following manner. By introducing the scaled quantities according to (27) into (13) and (14) we get

$$E_p^n = Z^{1+b+2a} E_p^{n'} \tag{28}$$

and

$$E_p^e = Z^{2b+5a} E_p^{e'}\,. \tag{29}$$

The normalization condition for the charge density turns out to be

$$-Ze = -e \int \varrho\, dv = Z^{b+3a}(-e) \int \varrho'\, dv' \tag{30}$$

for neutral atoms i.e. $N = Z$. If

$$b + 3a = 1 \tag{31}$$

the normalization condition

$$\int \varrho' \, dv' = 1 \tag{32}$$

is independent of the atomic number.

We may observe that because of equation (31) we get

$$c = 1 + b + 2a = 2b + 5a \tag{33}$$

for any value of a and the corresponding value of b.

Because of the virial theorem there is a scaling of the kinetic energy too

$$E_k = Z^c E'_k \, . \tag{34}$$

The total energy has the following form

$$E = E_k + E_p^n + E_p^e = Z^c E', \tag{35}$$

where E' is a slowly varying function of Z. By comparing (26b) and (35) we get for the exponent the value

$$c = \frac{7}{3}, \tag{36}$$

and using this value of c in (33), combining it with (31) and solving the system of linear equations we get the constants

$$a = -\frac{1}{3} \quad \text{and} \quad b = 2. \tag{37}$$

These constants have the values well known for the scaling exponents in the Thomas–Fermi theory.

Let us make the further assumption that

$$E_k = \int \varepsilon_k(\varrho) \, dv, \tag{38}$$

i.e. the kinetic energy is expressible as a function of the particle density. If we take an energy density like

$$\varepsilon_k(\varrho) = \varkappa \varrho^\lambda \, , \tag{39}$$

which is the simplest possible form, we get

$$\lambda = \frac{5}{3} \tag{40}$$

if we take the scaling and (34) with the proper value of the constant c. We leave the determination of the constant $\varkappa$ to a later discussion.

The Thomas—Fermi equation

According to (35), (34), (13) and (14) the total energy of the atom may be written in the following form

$$E = \varkappa \int \varrho^{5/3}\, dv - Ze^2 \int \frac{\varrho(\mathbf{r})}{|\mathbf{r}-\mathbf{r}|}\, dv' + \frac{1}{2}\, e^2 \iint \frac{\varrho(\mathbf{r})\,\varrho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}\, dv\, dv'.$$

By the aid of an argument similar to that given by GOMBÁS in his famous book [3] we get the Thomas—Fermi expression

$$\varrho = \sigma_0 (V - V_0)^{3/2}, \qquad \sigma_0 = \left(\frac{3e}{5\varkappa}\right)^{3/2} \tag{41}$$

and combining this with Poisson's equation we obtain the Thomas—Fermi equation

$$\Delta\,(V - V_0) = 4\,\pi\sigma_0\, e(V - V_0)^{3/2} \tag{42}$$

and the scaled form of this is

$$\varphi'' = \frac{\varphi^{3/2}}{x^{1/2}} \tag{43}$$

with exactly the same boundary conditions that may be found in GOMBÁS's book. We shall not repeat them here. The solution of the scaled equation (43) is the same and has been tabulated in the article [4].

In (43)

$$x = \frac{r}{\mu} \tag{44}$$

with

$$\mu = \frac{1}{(4\,\pi\sigma_0)^{3/2}\, eZ^{1/3}}, \tag{45}$$

and

$$\varphi(x) = \frac{r}{Ze}\,(V - V_0). \tag{46}$$

In all the above expressions $\varkappa$ is a yet undetermined constant. It is interesting that without this constant it is possible to get an equation for the determination of φ, i.e. the potential field. This is a consequence of the inhomogeneity of equations (42) and (43).

The final determination of this parameter may be achieved by the aid of the energy expression (26b) and the virial theorem. By inserting ϱ from (41) into (38) with (39) and taking into account (46), (45) and (44) we get the following expression

$$\varkappa = \frac{9}{35}(4\pi)^{2/3}\,\frac{\varphi'(0)}{-0.712\,866}\,e^2 a_0 = 3.0963\,e^2 a_0 . \tag{47}$$

Discussion

The consequences of the change in the value of the parameter $\varkappa$ as compared to that for the free electron value

$$\varkappa_k = \frac{3}{10}(3\pi^2)^{2/3}\,e^2 a_0 = 2.871\,e^2 a_0$$

may be summarized as follows. Because μ is proportional to $\varkappa$, the density distribution gets looser giving a smaller magnitude for the potential energy of the atom and consequently reducing the average kinetic energy too. These energy reductions result in a reduction of the total energy which is very much welcome, but the reduction is not enough to get near to the experimental total energy. Naturally many of the shortcomings of the original Thomas–Fermi density distributions remain incorporated also in this model.

The main aim of this paper has been achieved, however, because we have demonstrated that we can get a model starting from the true zero-order solutions of the atomic problem, which has the main features of the original Thomas—Fermi theory without mentioning plane waves and statistics at all.

Now we are in a position to reinterpret our results in the following manner. The kinetic energy density function $\varepsilon(\varrho) = \varkappa\varrho^{5/3}$ with $\varkappa = \varkappa_k$ is a characteristic function of free electrons with mass m_0. According to the above theory a neutral atom may be believed to be composed of a nucleus and a cloud of quasi particles that imitate free electrons but with a reduced mass $m = \nu m_0$, where

$$\nu = \frac{\varkappa_k}{\varkappa} = \frac{2.871\,e^2 a_0}{3.0963\,e^2 a_0} = 0.9272 .$$

It is interesting to note that a much better agreement for the energy of atoms may be achieved if we suppose semiempirically that the effective mass of the quasi electrons is

$$m' = \nu' m_0 \quad \text{with} \quad \nu' = \frac{2.871\,e^2 a_0}{3.51997\,e^2 a_0} = 0.8156 .$$

LITERATURE

1. See e. g. D. LAYZER, Ann. Phys. (N. Y.) **8**, 271, 1959.
2. R. GÁSPÁR, Int. J. Quantum Chemistry, **1**, 139, 1967.
3. P. GOMBÁS: Die statistische Theorie des Atoms und ihre Anwendungen, Springer-Verlag, Wien, 1949.
4. P. GOMBÁS: Statistische Behandlung des Atoms, S. Flügge's Encyclopaedia of Physics, Bd. 36. p. 127.

НОВЫЕ ОБОСНОВАНИЯ МОДЕЛИ ТОМАСА—ФЕРМИ

Р. ГАШПАР

Резюме

Демонстрируется, что атомная модель, в которой нулевое приближение одноэлектронных орбиталей есть применение водородоподобных орбиталей, систематически ведет к модели, точно напоминающей модель Томаса—Ферми статистической теории.