Thomas-Fermi model: Nonextensive statistical mechanics approach

Evgeny Martinenko and Bhimsen K. Shivamoggi*
University of Central Florida, Orlando, Florida 32816-1364, USA
(Received 25 November 2003; published 14 May 2004)

In this paper, the Thomas-Fermi model for large atoms is reformulated by incorporating the nonextensive entropy prescription. The entropy nonextensivity contribution dominates the usual thermal correction term in the "low-temperature" limit. On the other hand, the entropy nonextensivity concept appears to provide a useful framework to describe the fractal nature of the Fermi surface in the nondegenerate case. Analytical calculations are given for some atomic properties, such as the total binding energy of the electrons in the atom. The nonextensivity of entropy is indicated to have the potential to provide a means to remedy one of the well-known weaknesses in the Thomas-Fermi model—the boundary effect. The virial theorem has been shown to be a robust result that holds also in the nonextensive entropy regime.

DOI: 10.1103/PhysRevA.69.052504 PACS number(s): 31.15.Bs, 31.10.+z

I. INTRODUCTION

The Thomas-Fermi statistical model (Thomas [1], Fermi [2]) of the atom provides a heuristic semiclassical method to describe the ground-state potential fields and charge densities in large atoms, metals, and in astrophysical objects such as neutron stars [3], [4]. Despite the crudeness of the physical approximation, the Thomas-Fermi model remains useful due to its simplicity and elegance and serves rather well as a starting point for the study of interacting many particle systems. In this model one starts with relations appropriate to the homogeneous electron gas obeying the Fermi-Dirac statistics and then uses a *local density approximation* to apply these to the inhomogeneous charge cloud. The electrostatic potential $V(\mathbf{r})$ of the system can be determined by solving Poisson's equation for $V(\mathbf{r})$. Though more than 75 years old the Thomas-Fermi model is still a subject of improvements (see Shivamoggi [5], and references therein).

One well-known weakness of the Thomas-Fermi model is that it describes incorrectly the innermost electrons that contribute most to the binding energy of the atom—the *boundary effect*. This defect may be traced to the fact that this model allows too great a density of electrons very close to the nucleus (the electron density in fact tends to infinity at the nucleus as $r^{-3/2}$) thereby causing a breakdown of the local-density approximation near the nucleus. This defect leads to predictions of the total binding energy of the atom that are higher than the experimental binding energies derived from spectroscopy.

In dealing with the statistical properties of systems with long-range interactions,[1] it has been proven useful to extend Boltzmann-Gibbs thermodynamics by generalizing the concept of entropy to nonextensive regimes (Tsallis [9], see Ref. [10] for an extensive bibliography on the theory and applications). This nonextensive thermostatistical prescription has been shown [11,12] to afford a consistent thermodynamic description of such systems. It is therefore of interest to reformulate the Thomas-Fermi model for an atom with thermal effects by incorporating the nonextensive entropy prescription [13] and to explore whether this approach provides a remedy for the above-mentioned weakness of the Thomas-Fermi model.

II. NONEXTENSIVE THERMOSTATISTICS

Tsallis's nonextensive thermostatistics is based on two postulates [9]:

(1) The entropy of the system is given by

$$S^{(q)} = k_b \frac{1 - \sum_{i=1}^{W} p_i^q}{q - 1}, \tag{1}$$

(2) the expectation value of an observable A is

$$\langle A \rangle = \frac{\sum_{i=1}^{W} A_i p_i^q}{\sum_{i=1}^{W} p_i^q}, \tag{2}$$

where q is the nonextensivity parameter, $p_i : \Sigma_{i=1}^{W} p_i = 1$ are probabilities of the microstate (see [12] for a discussion), and k_b is a constant.

Maximizing (1) subject to constraints of conservation of total energy and the number of particles one may derive for the Fermion distribution function [12] and [14]:

*Electronic address: bhimsens@pegasus.cc.ucf.edu

[1] Generalization of Boltzman-Gibbs thermodynamics has also been found useful in dealing with multifractal properties of systems (Beck [6], Shivamoggi and Beck [7], and Shivamoggi [8]).

$$f^{(q)}(E) = \begin{cases} \dfrac{1}{1+[1+(q-1)\beta(E-\mu)]^{q/q-1}} & \text{if } 1+(q-1)\beta(E-\mu)>0, \\ 1 & \text{otherwise}. \end{cases} \tag{3}$$

Here, $\beta \equiv 1/k_b T$ and $q>1$. In the limit $q\to 1$, (1) reduces to the familiar Shannon entropy function,

$$\lim_{q\to 1} S^{(q)} = -k_b \sum_{i=1}^{W} p_i \ln p_i, \tag{4}$$

and Eq. (3) reduces to the familiar Fermi-Dirac distribution,

$$\lim_{q\to 1} f^{(q)}(E) = \frac{1}{e^{\beta}(E-\mu)+1}. \tag{5}$$

Figure 1 shows a plot of $f^{(q)}(E)$ for different values of q, with $\mu=5$ eV and $T=300$ K. Figure 2 shows a plot of $f^{(q)}(E)$ for different values of T, with $\mu=5$ eV and $q=1.1$. As one can see in the zero temperature limit, Eq. (3) will reduce to the step function corresponding to an ideal degenerate Fermi gas. On the other hand, with T kept fixed, increasing q will make the distribution $f^{(q)}(E)$ steeper. It has apparently the same effect as that produced by reducing T (see Fig. 3). In fact, the slope of $f^{(q)}(E)$ at $f^{(q)}(E)=0.5$ is equal to $-q\beta/4$, so "nonextensivity" seems to increase the degree of degeneracy. This of course supports the viewpoint that q is a measure of the correlation in the system.

III. THOMAS-FERMI MODEL BASED ON THE TSALLIS FORMALISM

Rewriting (3) as a function of momentum we obtain for the electron number density

$$n = \frac{1}{\pi^2\hbar^3}\int_0^\infty \frac{p^2 dp}{1+\left\{1+(q-1)\beta\left[\dfrac{p^2}{2m}-eV(r)-\mu\right]\right\}^{q/(q-1)}},$$

$$1+(q-1)\beta\left[\frac{p^2}{2m}-eV(r)-\mu\right]>0. \tag{6}$$

Using Eq. (6) in the Poisson equation

$$\nabla^2 V = 4\pi e n, \tag{7}$$

and assuming spherical symmetry, we obtain a generalized Thomas-Fermi equation

$$\frac{1}{r}\frac{d^2(rV)}{dr^2} = \frac{2}{\pi\hbar^3} e(2m\beta)^{3/2}\Theta_{1/2}^{(q)}(\beta\{eV(r)-\mu\}), \tag{8}$$

where the function $\Theta_n^{(q)}(y)$ is defined by

$$\Theta_n^{(q)}(y) = \int_0^\infty \frac{t^n}{1+[1+(q-1)(t-y)]^{q/(q-1)}} \times H(1+(q-1)(t-y))dt, \tag{9}$$

$H(x)$ being the Heaviside step function.

Integration by parts yields

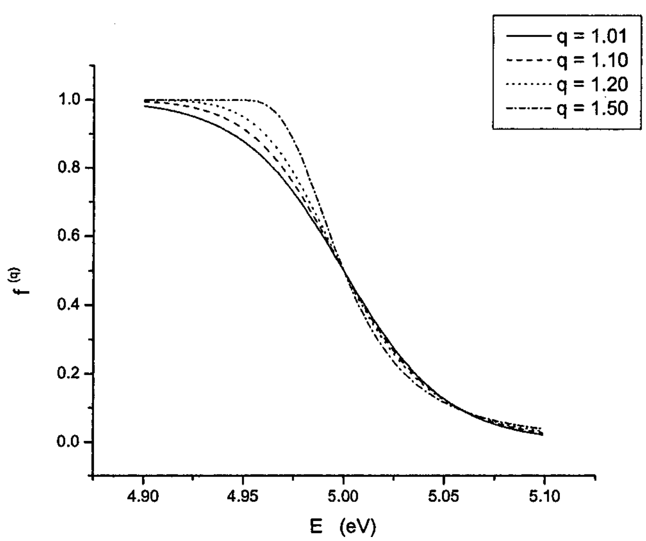

FIG. 1. Plot of $f^{(q)}$ vs E for $\mu=5$ eV and $T=300$ K.

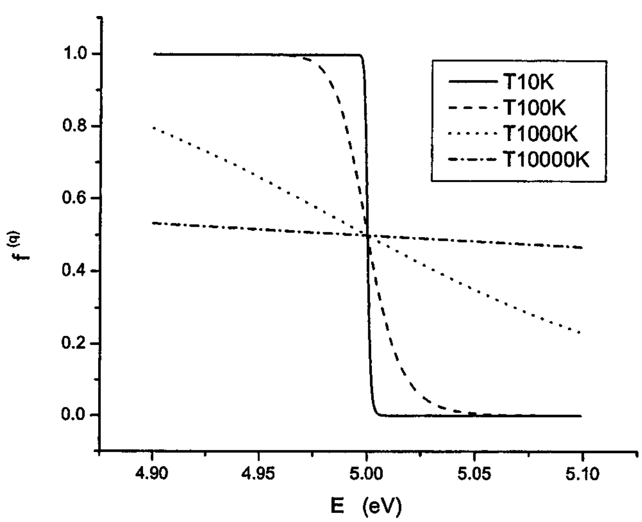

FIG. 2. Plot of $f^{(q)}$ vs E for $\mu=5$ eV and $q=1.1$.

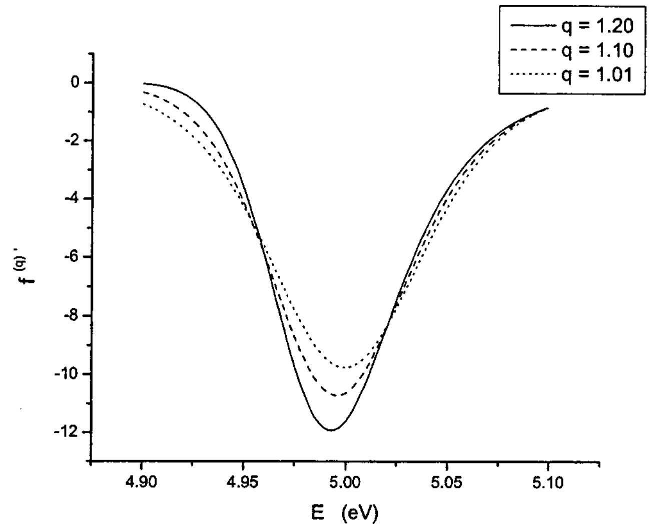

FIG. 3. Plot of $f^{(q)\prime}$ vs E for $\mu=5$ eV and $T=300$ K.

$$\Theta_n^{(q)}(y) = \frac{q}{n+1}\int_0^\infty \frac{t^{n+1}[1+(q-1)(t-y)]^{1/(q-1)}}{\{1+[1+(q-1)(t-y)]^{q/(q-1)}\}^2} \times H(1+(q-1)(t-y))dt. \tag{10}$$

Setting $z \equiv t-y$, we obtain for weak-thermal effects (i.e., $|y| \gg 1$),

$$\Theta_n^{(q)}(y) = \frac{q}{n+1}y^{n+1}\int_{-\infty}^\infty \frac{\left(1+\frac{z}{y}\right)^{n+1}[1+(q-1)z]^{1/(q-1)}}{\{1+[1+(q-1)z]^{q/(q-1)}\}^2} \times H(1+(q-1)z)dz. \tag{11}$$

Further, expanding $[1+(z/y)]^{n+1}$ in powers of z/y we obtain

$$\Theta_n^{(q)}(y) = \frac{1}{n+1}y^{n+1}I_0^{(q)} + y^n I_1^{(q)} + \frac{n}{2}y^{n-1}I_2^{(q)} + \cdots, \tag{12}$$

where

$$I_n^{(q)} = q\int_{-\infty}^\infty \frac{z^n[1+(q-1)z]^{1/(q-1)}}{\{1+[1+(q-1)z]^{q/(q-1)}\}^2}H(1+(q-1)z)dz. \tag{13}$$

Now, Eq. (8) can be simplified using Eq. (12) and making the following change of variables:

$$r \equiv bx, \quad V(r) - \mu \equiv \frac{Ze^2\Phi}{r},$$

where Z is the atomic number, and

$$b \equiv \frac{\pi^{2/3}3^{2/3}}{2^{7/3}}\frac{\hbar^2}{[I_0^{(q)}]^{2/3}Z^{1/3}m_e e^2}, \quad \tilde{v} \equiv \frac{3}{2}k_b T\frac{I_1^{(q)}b}{I_0^{(q)}e^2 Z}, \tag{14}$$

$$v \equiv \frac{3}{8}(k_b T)^2\frac{I_2^{(q)}b^2}{I_0^{(q)}e^4 Z^2},$$

we then obtain

TABLE I. Values for the first two integrals $I_n^{(q)}$ estimated numerically.

q	$I_1^{(q)}$	$I_2^{(q)}$
1.01	0.016	3.228
1.05	0.075	3.039
1.10	0.137	2.907
1.20	0.236	2.870
1.50	0.488	4.000

$$\frac{d^2\Phi}{dx^2} = \frac{\Phi^{3/2}}{\sqrt{x}}\left[1 + \tilde{v}\frac{x}{\Phi} + v\left(\frac{x}{\Phi}\right)^2\right]. \tag{15}$$

Observe the appearance of a Tsallis correction term, namely, the one with $\tilde{v}$ in the Thomas-Fermi equation. Note that the Tsallis correction term is proportional to $k_b T$ whereas the usual thermal-correction term … [15], namely, the one with v, is proportional to $(k_b T)^2$. So, $v \ll \tilde{v} \ll 1$, in the "low-temperature"[2] limit and the Tsallis correction term dominates the usual thermal correction term in this limit.

Equation (15) may therefore be approximated by

$$\frac{d^2\Phi}{dx^2} = \frac{\Phi^{3/2}}{\sqrt{x}}\left(1 + \tilde{v}\frac{x}{\Phi}\right). \tag{16}$$

The Tsallis correction also leads to the q-dependent integrals in the scaling factors in (14). The integral $I_0^{(q)}$ is, however, easily calculated and can be shown to be identically equal to 1; therefore, the Tsallis correction vanishes when $T=0$, as to be expected. Thus, following the general ideas in [6], [7], and [8], the entropy nonextensitity appears to provide a useful framework to describe the fractal nature of the Fermi surface in the nondegenerate case. Table I presents values for the first two integrals $I_n^{(q)}$ estimated numerically (such an evaluation was also done by Torres and Tirnakli [16]).

One notices that $I_1^{(q)}$ tends to vanish with $q \to 1$, as it should. To highlight the q dependence of $I_n^{(q)}$, (13) can be written as

$$I_n^{(q)}\int_{-\infty}^\infty z^n \xi(z,q)dz, \tag{17}$$

where

$$\xi(z,q) = \frac{q[1+(q-1)z]q^{1/(q-1)}}{\{1+[1+(q-1)z]q^{q/(q-1)}\}^2}H[1+(q-1)z].$$

Differentiating $\xi(z,q)$ over q and evaluating the first two derivatives for $q=1$, we have

$$\left.\frac{\partial\,\xi(z,q)}{\partial q}\right|_{q=1} = \frac{e^z}{(1+e^z)^2} - \frac{e^2 z^2}{2(1+e^z)^2} + \frac{ze^{2z}(z-2)}{(1+e^z)^3},$$

[2]The "low-temperature" actually refers to temperatures of $O(10^6$ K). The concomitant thermal effects are still small because of the very large Fermi energy in cases of interest.

$$\left.\frac{\partial\,\xi(z,q)}{\partial\,q^2}\right|_{q=1}=\frac{e^z z^2}{(1+e^z)^2}+\frac{2e^{2z}(z-2)}{(1+e^z)^3}+\frac{e^z z^4}{4(1+e^z)^2}+\frac{2e^z z^3}{3(1+e^z)^2}-\frac{e^z z^2(z-2)}{(1+e^z)^3}+\frac{\frac{3}{2}z^2e^{3z}(z^2-4z+4)}{(1+e^z)^4}-\frac{1}{2}\frac{z^2e^{2z}(z^2-4z+4)}{(1+e^z)^3}-\frac{2}{3}\frac{e^{2z}z^2(-3+2z)}{(1+e^z)^3}, \tag{18}$$

etc. Using these results we obtain from Eq. (17)

$$I_1^{(q)}=\frac{\pi^2}{6}(q-1)-\frac{2\pi}{3}(q-1)^2+O((q-1)^3),$$

$$I_2^{(q)}=\frac{\pi^2}{3}-\frac{2\pi^2}{3}(q-1)-\frac{229\pi^2}{90}(q-1)^2+O((q-1)^3), \tag{19}$$

etc.

Observe that, using Eqs. (14) and (19), Eq. (15) reduces, in the limit $q\to 1$, to the Marshak-Bathe [15] equation

$$\frac{d^2\phi}{dx^2}=\frac{\Phi^{3/2}}{\sqrt{x}}\left[1+v\left(\frac{x}{\Phi}\right)^2\right]. \tag{20}$$

IV. VIRIAL THEOREM

Following Feynman, Metropolis, and Teller [17], consider the kinetic energy of all electrons in some atom with radius a:

$$E_{\text{kin}}=\frac{16\pi^2}{h^3m}\int_0^a r^2dr\int_0^\infty\frac{p^4dp}{1+\left[1+(q-1)\left(\beta\frac{p^2}{2m}-\eta\right)\right]^{q/(q-1)}}, \tag{21}$$

where

$$\eta\equiv\beta[eV(r)-\mu].$$

Setting

$$y\equiv\beta\frac{p^2}{2m}, \tag{22}$$

Eqs. (21) and (6) become

$$E_{\text{kin}}=\frac{(2mk_b)^{5/2}}{\pi\hbar^3m}\int_0^a r^2dr\int_0^\infty\frac{y^{3/2}dy}{1+[1+(q-1)(y-\eta)]^{q/(q-1)}}, \tag{23}$$

$$n=\frac{(2mk_b)^{3/2}}{2\pi^2\hbar^3m}\int_0^\infty\frac{y^{1/2}dy}{1+[1+(q-1)(y-\eta)]^{q/(q-1)}}. \tag{24}$$

Integrating Eq. (23) by parts, first with respect to r, and then again with respect to y, and using Eq. (24), we obtain

$$E_{\text{kin}}=\frac{a^3(2mk_b)^{5/2}}{3\pi\hbar^3m}\int_0^\infty\frac{y^{3/2}dy}{1+[1+(q-1)(y-\eta^*)]^{q/(q-1)}}-2\pi e\int_0^a r^3\frac{\partial V}{\partial r}n(r)dr, \tag{25}$$

where η^* is the value of η at the surface of the atom.

Computing the pressure at the surface as the momentum carried across this surface in unit time per unit area, we have

$$P=\frac{2}{h^3}\int_0^\infty\frac{4\pi\frac{1}{3}p\left(\frac{p}{m}\right)p^2dp}{1+\left[1+(q-1)\left(\beta\frac{p^2}{2m}-\eta^*\right)\right]^{q/(q-1)}}$$

or

$$P=\frac{(2mk_b)^{5/2}}{6\pi^2\hbar^3m}\int_0^\infty\frac{y^{3/2}dy}{1+[1+(q-1)(y-\eta^*)]^{q/(q-1)}}. \tag{26}$$

The first term in Eq. (25) can then be expressed as $3P\mathcal{V}/2$ where $\mathcal{V}$ is the atomic volume $\mathcal{V}=4/3\pi r^3$. To evaluate the second term in Eq. (25), note that Eq. (7) and the spherical symmetry assumption will lead to

$$n=\frac{V''+\frac{2}{r}V'}{4\pi e}. \tag{27}$$

We have for the potential energy of all atomic electrons

$$E_{\text{pot}}=\frac{4\pi e}{2}\int_0^a V(r)n(r)r^2dr. \tag{28}$$

Using Eqs. (27) and (28) leads to

$$2\pi e\int_0^a r^3\frac{\partial V}{\partial r}n(r)dr=\frac{E_{\text{pot}}}{2}. \tag{29}$$

Using Eqs. (25), (26), and (29), we obtain the virial theorem

$$2E_{\text{kin}}+E_p=3P\mathcal{V},\quad \forall\, q\geqslant 1. \tag{30}$$

Thus, the virial theorem is a robust result that is not altered by the nonextensivity of entropy.

V. BINDING ENERGY OF AN ATOM

The virial theorem (30) shows that the total binding energy $-E$ of the atom is equal to the total kinetic energy. Using Eqs. (9) and (23) becomes

$$E_{\mathrm{kin}} = \frac{(2mk_b)^{5/2}}{\pi\hbar^3 m}\int_0^\infty \Theta_{3/2}^{(q)}(\eta) r^2 dr. \quad (31)$$

Using the same approach as in [5], and expanding Θ, under the weak-thermal effect condition, we have from Eq. (12),

$$\Theta_{3/2}^{(q)}(\eta) = \frac{2}{5}\eta^{5/2} + \eta^{3/2} I_1^{(q)} + \cdots. \quad (32)$$

Using Eq. (32) and the truncated Thomas-Fermi equation (16), and scaling the variables as per (14), we obtain

$$E_{\mathrm{kin}} = \frac{3}{5}\frac{e^2Z^2}{b}\int_0^\infty \frac{\Phi^{5/2}}{\sqrt{x}}dx + \frac{3}{2}I_1^{(q)} Z k_b T \int_0^\infty \Phi^{3/2}\sqrt{x}dx. \quad (33)$$

After integration by parts and some algebra we obtain the result for the binding energy of the atom

$$E_b = -\frac{3}{7}\frac{e^2Z^2}{b}\left[-\Phi'(0) - \frac{2}{3}\tilde{v}\right] + O(\tilde{v}^2). \quad (34)$$

Equation (34) shows that E_b is reduced by the nonextensive entropy effect $q > 1$. Thus, the nonextensivity of entropy appears to provide a means to remedy the *boundary effect*.

VI. DISCUSSION

In the present paper we have reformulated the Thomas-Fermi model by incorporating the nonextensive entropy prescription. The entropy nonextensivity contribution dominates the usual thermal correction term in the "low-temperature" limit. On the other hand, the entropy nonextensivity concept appears to provide a useful framework to describe the fractal nature of the Fermi surface in the nondegenerate case. We have given generalization of the Thomas-Fermi equation for the nonextensive entropy cases. The nonextensive entropy corrections vanish in the zero-temperature limit, as to be expected. However, in the low-temperature limit, the nonextensive entropy corrections dominate the usual thermal corrections. We also have shown that the virial theorem is a robust result that continues to hold also in the nonextensive entropy regime. We have made analytical calculations of some atomic properties as the binding energy of the electrons in the atoms and have found that the binding energy is reduced by the nonextensive entropy effects. So, the nonextensivity of entropy appears to provide a means to remedy the boundary effect. However, quantitative comparison of Eq. (34) with experimental data at this time appears to be difficult because binding energies of neutral atoms for $Z > 20$ are rarely known experimentally (Englert [18]).

ACKNOWLEDGMENTS

The authors are grateful to Professor Constantino Tsallis for his helpful suggestions, and Professor Michael Johnson for his careful scrutiny of the manuscript.

[1] L. H. Thomas, Proc. Cambridge Philos. Soc. **33**, 542 (1927).
[2] E. Fermi, Rend. Accad. Naz. Lincei **6**, 602 (1928).
[3] P. Gombas, *Die Statistiche Theoris des Atoms und Ihre Anwendungen* (Springer, Wien, 1949).
[4] L. Spruch, Rev. Mod. Phys. **63**, 152 (1991).
[5] B. K. Shivamoggi, Phys. Rev. A **51**, 185 (1995).
[6] C. Beck, Physica A **277**, 115 (2000).
[7] B. K. Shivamoggi and C. Beck, J. Phys. A **34**, 4003 (2001).
[8] B. K. Shivamoggi, Physica A **318**, 358 (2003).
[9] C. Tsallis, J. Stat. Phys. **52**, 479 (1998).
[10] C. Tsallis, in *Nonextensive Statistical Mechanics and Thermodynamics*, edited by S. Abe and Y. Okamoto, Lecture Notes in Physics (Springer, Berlin, 2001).
[11] E. M. F. Curado and C. Tsallis, J. Phys. A **24**, 69 (1991).
[12] C. Tsallis, R. Mendes, and A. R. Plastino, Physica A **261**, 534 (1998).
[13] E. Martinenko and B. K. Shivamoggi, Bull. Am. Phys. Soc. **47**, 71 (2002).
[14] I. S. Olivera, Eur. Phys. J. B **14**, 43 (2000).
[15] R. F. Marshak and M. Bethe, Astrophys. J. **91**, 239 (1940).
[16] D. F. Torres and U. Tirnakli, Physica A **261**, 499 (1998).
[17] R. Feynman, N. Metropolis, and E. Teller, Phys. Rev. **75**, 1561 (1949).
[18] B. G. Englert, *Semiclassical Theory of Atoms*, Springer Lecture Notes in Physics Vol. 300 (Springer-Verlag, New York, 1988).