Journal of Theoretical Physics

Quasi-classical atoms, ions and atomic clusters

M. Apostol
Department of Theoretical Physics,
Institute of Atomic Physics,
Magurele-Bucharest MG-6, POBox MG-35, Romania
email:apoma@theory.nipne.ro

Abstract

Since the quasi-classical approximation for atoms and ions holds over a moderate range of distances, a linear version of the Thomas-Fermi model is devised, which is more practical. The theory is applied to the atomic stability, ionization potential, electron affinity and atomic plasmons, as well as to similar questions for a spherical-shell model of clusters, where the typical molecular vibrations are also given; the magnetic moment, diamagnetic susceptibity and electric polarizability are also computed in the latter case. Various extensions of, and improvements upon, the shell-cluster model are discussed, including the treatment of the discrete geometrical structure.

According to the quasi-classical approximation a quantal particle moves in an external potential energy ε_{pot} such that

$$\varepsilon_{kin} + \varepsilon_{pot} = const \quad , \tag{1}$$

where ε_{kin} is the kinetic energy of the particle; the motion is described by a quasi-plane wave-function, with a certain (quasi-) momentum, and the approximation is valid as long as the spatial variations of the wavelength are small; this is so for potentials which vary slightly over particle wavelength in comparison with the particle energy. For quasi-classical electrons in an electrostatic potential $\varphi(\mathbf{r})$ the above equation reads

$$\varepsilon_F - e\varphi = -e\varphi_0 \quad , \tag{2}$$

where ε_F is the Fermi energy, $-e$ is the electron charge, and the constant in (1) has been denoted by $-e\varphi_0$ for convenience (obviously, it plays the part of a chemical potential); for a neutral atom $\varphi_0 = 0$, since the electrons are bound and φ vanishes at infinite, while for a positive ion $\varphi_0 > 0$, because the field does not vanish at infinite; in this latter case $\varepsilon_F = e(\varphi - \varphi_0)$ vanishes at some boundary, and it is assumed to remain zero beyond this boundary; a positive ion has a finite extension, in contrast with a neutral one, which extends up to infinite; a similar situation occurs for a negative ion, where, however, a potential barrier appears, in addition. Equation (2) can also be written as

$$\frac{\hbar^2}{2m}k_F^2 - e\varphi = -e\varphi_0 \quad , \tag{3}$$

where k_F is the Fermi wavevector, and m denotes the electron mass. Since $e(\varphi - \varphi_0)$ varies slightly we may replace k_F^2 in the equation above by $k_F \delta k_F$, where the parameter k_F has to be determined; this linearization is a good approximation as long as k_F is comparable with δk_F; consequently, equation (3) becomes

$$\frac{\hbar^2}{2m}k_F \delta k_F - e\varphi = -e\varphi_0 \quad . \tag{4}$$

Similarly, for the electron density $n = k_F^3/3\pi^2$ we may use the linearized formula

$$n = \frac{1}{3\pi^2}k_F^2\delta k_F \quad , \tag{5}$$

and

$$E_{kin} = \frac{\hbar^2 k_F^4}{10\pi^2 m}\int d\mathbf{r} \cdot \delta k_F \tag{6}$$

for the corresponding kinetic energy $E_{kin} = (V/10\pi^2 m)\hbar^2 k_F^5$, where V denotes the volume. The electric potential satisfies the Poisson's equation

$$\Delta\varphi = -4\pi eZ\delta(\mathbf{r}) + 4\pi en \tag{7}$$

for a nuclear charge Ze placed at the origin; substituting δk_F from (4) in (5) the Poisson's equation becomes

$$\Delta\varphi = -4\pi eZ\delta(\mathbf{r}) + \frac{8me^2}{3\pi\hbar^2}k_F\left(\varphi - \varphi_0\right) \quad , \tag{8}$$

which, in contrast to the usual Thomas-Fermi model for atoms,[1] is a linear equation.

For a neutral atom $\varphi_0 = 0$ and φ vanishes at infinite; the above equation can be solved by a Fourier transform; one obtains

$$\left(k^2 + q^2\right)\varphi(\mathbf{k}) = eZ/2\pi^2 \quad , \tag{9}$$

where

$$q = (8me^2 k_F/3\pi\hbar^2)^{1/2} \tag{10}$$

is a Thomas-Fermi screening wavevector. The solution is the screened Coulomb potential

$$\varphi = \frac{Ze}{r}e^{-qr} \quad ; \tag{11}$$

one can check that the total number of electrons is

$$\int d\mathbf{r} \cdot n = \int d\mathbf{r} \cdot \frac{2mek_F}{3\pi^2\hbar^2}\varphi = q^2 Z\int dr \cdot re^{-qr} = Z \quad , \tag{12}$$

as it should be, according to the boundary conditions of the neutral atom. The kinetic energy (6) is

$$E_{kin} = \frac{4k_F^3}{5\pi}\frac{Ze^2}{q^2} = \frac{4}{5\pi}\left(\frac{3\pi\hbar^2}{8me^2}\right)^3 Ze^2 q^4 \quad , \tag{13}$$

while the potential energy is given by

$$E_{pot} = \int d\mathbf{r} \cdot \left(\rho_e\varphi - \frac{1}{2}\rho_e\varphi_e\right) = \frac{1}{2}\int d\mathbf{r} \cdot \left(\rho_e\varphi + \rho_e\varphi_c\right) \quad , \tag{14}$$

where $\rho_e = -en$ is the density of the electron charge, φ_e is the electrons field and $\varphi_c = Ze/r$ is the nuclear (core) field; from (14) one gets

$$E_{pot} = -\frac{3}{4}Z^2 e^2 q \quad . \tag{15}$$

The total energy $E_{kin} + E_{pot}$ has a minimum value for

$$q = \frac{2}{3\pi}(15\pi Z)^{1/3}\frac{me^2}{\hbar^2} = 0.77Z^{1/3}\frac{me^2}{\hbar^2} \quad , \tag{16}$$

which determines the parameter

$$k_F = \frac{1}{6\pi}(15\pi Z)^{2/3}\frac{me^2}{\hbar^2} \quad ; \tag{17}$$

(it may be taken as a measure of the average electron density of the atom, $n = k_F^3/3\pi^2 \sim Z^2$); the minimum value of the energy is

$$E_b = -\frac{9}{16}Z^2e^2q = -\frac{3}{4\pi}Z^2(15\pi Z)^{1/3}\text{ry} = -11.7Z^{7/3}\text{eV} \quad , \tag{18}$$

where ry denotes the rydberg $e^2/2a_H = 13.6\text{eV}$, and $a_H = \hbar^2/me^2 = 0.53\text{Å}$ is the Bohr radius. This E_b is the binding energy of the atom; it compares well with the empirical value $16Z^{7/3}\text{eV}$, and it is a counter-balancing approximation in comparison with the non-linear Thomas-Fermi model which gives $20.8Z^{7/3}\text{eV}$. The variation δk_F is comparable with the parameter k_F over a distance $R \sim 1/q \sim Z^{-1/3}$ (in Bohr radii), which may be taken as the "radius" of the atom (indeed, the radial density of electrons has a maximum value for $R = 1/q$; also, the electron velocity is of the order of $Z^{2/3}$); it is precisely such a moderate distance over which the quasi-classical approximation is valid; indeed, as it is well known, the quasi-classical approximation holds for distances longer than $1/Z$, which is the radius of the first Bohr orbit, where the quantal corrections matter (the corresponding delocalization energy being responsible for correcting the Thomas-Fermi result), and shorter than 1, beyond which the wavelength becomes much longer than the range $(1/q)$ of the potential; from these conditions one can see that the quasi-classical approximation holds for large atomic numbers Z; accordingly, the "size" of the atoms does not depend on Z, the electrons being localized between $1/Z$ and 1, which agrees satisfactorily with the empirical data.

The potential energy of the electrons in the nuclear (core) field is $E_{ec} = -Z^2e^2q$, according to the above computations, while the Coulomb repulsion between electrons is $E_{ee} = E_{pot} - E_{ec} = (1/4)Z^2e^2q$ (from (15), which gives $E_{pot} = -(3/4)Z^2e^2q$); on the other hand, the kinetic energy is $E_{kin} = (3/16)Z^2e^2q$, at equilibrium; one can see that $2E_{kin} = -(1/2)E_{pot}$, which is in contrast with the virial theorem that requires $2E_{kin} = -E_{pot}$; this is not unexpected, as long as the linear approximation employed here destroys the quadratic dependence of energy on momentum, and introduces an undefinite momentum distribution of electron states. However, this circumstance does not affect much the numerical computations; in addition, it is worth noting that the atom within the linear approximation is "spongier" over short and medium distances in comparison with the non-linear Thomas-Fermi model, *i.e.* the electrons are farther away from the nucleus within the linear approximation; this may explain the numerical discrepancy between the two approaches.

The virial theorem offers the opportunity of correcting the linear approximation; indeed, since the electron density must be increased, then a kinetic energy δE_{kin} and a potential energy δE_{pot} must be added to the total energy; on the other hand, the virial theorem requires $2(E_{kin} + \delta E_{kin}) = -E_{pot} - \delta E_{pot}$, and, since $2E_{kin} = -(1/2)E_{pot}$, one obtains $2\delta E_{kin} + \delta E_{pot} = -(1/2)E_{pot} = 2E_{kin}$; according again to the virial theorem this latter quantity should vanish, which means that the computations are affected by an error of the order of E_{kin}; indeed, substracting E_{kin} from the binding energy (18) one obtains the corrected binding energy $E_b' = E_{pot} = (4/3)E_b = -15.6Z^{7/3}\text{eV}$, which agrees very well with the empirical data. A similar correction to the non-linear Thomas-Fermi model (which overestimates the binding energy) would require an addional E_{kin} to the binding energy, which lowers the coefficient 20.8 to 16.9. In general, the non-linear Thomas-Fermi model overestimates the quantal corrections, with its strong variations over short distances, while

its linear version underestimates these effects, as a consequence of the smother variations; the actual numbers should therefore lie between the results of these two computations. As a matter of fact, the first-order correction to the electron energies should be included within the perturbation theory for the potential φ, in order to get an improved accuracy.

The quasi-classical approximation amounts to the Hartree approximation for Coulomb interaction between electrons and the external Coulomb field of the nucleus; the results should be corrected for the exchange Coulomb interaction; as it is well known, this exchange interaction is given by $E_{ex} = -(1/4\pi^3)Ve^2k_F^4$; according to the linearization prescription it may also be written as

$$E_{ex} = -\frac{1}{4\pi^3}e^2k_F^3 \int d\mathbf{r} \cdot \delta k_F \quad ; \tag{19}$$

it is easy to see that it brings a Zq^2-correction to the energy; this correcting term can be treated perturbationally, and one can see easily that its effect is of the order of $Z^{-2/3}$ in comparison with the main contribution; the energy is therefore corrected by a $Z^{5/3}$-term, which is too small to be taken into account here. Therefore, one may neglect the exchange energy in such computations.

Let $\delta n(\mathbf{r})$ be a variation of the electron density (*i.e.* of δk_F in (5)), such that $\int d\mathbf{r} \cdot \delta n(\mathbf{r}) = 0$; the kinetic energy (6) brings no contribution to the change in the total energy, and, in fact, only the term $\rho_e\varphi$ in (14) gives a potential energy

$$U = -\frac{2\pi e^2}{q^2} \int d\mathbf{r} \cdot (\delta n)^2 \tag{20}$$

(the terms linear in δn bring not an important contribution for the present discussion); the variation of density is related to a displacement field $\mathbf{u}$ by $\delta n = -div(n\mathbf{u})$, which leads to the hamiltonian

$$H = \int d\mathbf{r} \cdot \left[\frac{1}{2}m \overset{\bullet}{u}^2 n - \frac{2\pi e^2}{q^2}(divn\mathbf{u})^2 \right] \quad ; \tag{21}$$

the corresponding equation of motion can be written as

$$\overset{\bullet\bullet}{f} = (2\pi e^2/mq^2)n\Delta f \quad , \tag{22}$$

for any component f of $n\mathbf{u}$; the frequency ω can be found by Fourier transform,

$$\omega^2 f(\mathbf{k}) = \frac{Ze^2}{4\pi^2 m} \int d\mathbf{k}' \cdot f(\mathbf{k}') \frac{k'^2}{(\mathbf{k} - \mathbf{k}')^2 + q^2} \quad . \tag{23}$$

For small $\mathbf{k}$ the function f has a range of the order of q, so that we obtain $\omega^2 \sim Ze^2q^3/m$; hence, $\hbar\omega \sim 13.6Z$eV, which is the frequency of the density waves in the atom, *i. e.* of the atomic plasmons. A similar estimation can be made directly in (22) for $\int d\mathbf{r} \cdot f$, by using the Poisson's equation.

We may add the centrifugal potential energy $E_{cf} = \hbar^2(l+1/2)^2/2mr^2$ to the potential energy $-e\varphi$, as given by (11), (where the quasi-classical orbital momentum $l + 1/2$ is used for $(l^2 + l)^{1/2}$), and look for the occurence of various l-states; this requires obviously $E_{cf} = -e\varphi$ and $E'_{cf} = -e\varphi'$; one obtains $Z = 0.13(2l+1)^3$, as compared with the non-linear Thomas-Fermi result $Z = 0.15(2l+1)^3$; for $Z = 0.17(2l + 1)^3$ one gets the atomic shell-model numbers $Z = 5$ for $l = 1$, $Z = 21$ for $l = 2$, $Z = 58$ for $l = 3$, etc (in agreement with the empirical data).

The Poisson's equation (8) can also be rewritten as $\Delta\varphi = q^2(\varphi - \varphi_0)$ and the condition $\varphi \sim Ze/r$ for $r \to 0$; the solution is $\varphi = \varphi_0 + (Ze/r)e^{-qr}$; this is helpful for positive ions, where the electrons

may be viewed as being confined, more or less, to a certain finite region around the nucleus; inside this region the potential is $\varphi = \varphi_0 + (Ze/r)e^{-qr}$, while at large distances the potential is $\varphi = ze/r$, where ze denotes the positive charge of the ion; we shall assume $z = 1$, and the continuity conditions read

$$\varphi_0 R_1 + Zee^{-qR_1} = e \ , \quad Z(1 + qR_1)e^{-qR_1} = 1 \ , \tag{24}$$

for a certain radius R_1 to be determined (together with the constant φ_0). For large atomic numbers Z (beyond 10) the solution to the second equation in (24) can be represented as $qR_1 = \ln Z + \beta$, where β is a slowly increasing function of Z (from ~ 1.6 for $Z \sim 10$ to 2 for large Z). The constant φ_0 is therefore $\varphi_0 = eq/(1 + qR_1) \simeq eq/(\ln Z + \beta + 1)$; $-e\varphi_0$ is the highest occupied level of electron energy in the ion. The potential determined above is an approximate potential, and the actual radius of the ion is determined by $\varphi = \varphi_0$; making use of the potential given above, one obtains $qR_2 = 1 + qR_2 = \ln Z + \beta + 1$; we take a mean value between R_1 and R_2 as the actual radius R, which is given by $qR = \ln Z + \beta + 1/2$; similarly, the constant φ_0 should be slightly higher, and we shall take for it the mean value $\varphi_0 = eq/R \simeq eq/(\ln Z + \beta + 1/2) = \alpha eq$, where $\alpha = (\ln Z + \beta + 1/2)^{-1}$. Under these conditions the kinetic energy is

$$E_{kin} = \frac{4}{5\pi} \left(\frac{3\pi\hbar^2}{8me^2} \right)^3 Ze^2q^4 \left[1 - (1 + q^2)e^{-qR} \right] \ , \tag{25}$$

or

$$E_{kin} = AZe^2q^4 - A\gamma e^2q^4(1 + q^2) \ , \tag{26}$$

where $A = (4/5\pi)(3\pi\hbar^2/8me^2)^3$ and $\gamma = (2.73)^{-\beta-1/2}$. The potential energy is given by

$$E_{pot} = -\frac{3}{4}Z^2e^2q - \frac{1}{2}Ze\varphi_0 + \frac{1}{4}Z^2e^2q(e^{-qR} + 2)e^{-qR} + \frac{1}{2}Ze\varphi_0(1 + q^2)e^{-qR} \ , \tag{27}$$

or

$$E_{pot} = -\frac{3}{4}Z^2e^2q - \frac{1}{2}(\alpha - \gamma)Ze^2q + \frac{1}{4}\gamma e^2q \left[\gamma + 2\alpha(1 + q^2) \right] \ . \tag{28}$$

The minimum value of the total energy can be found by looking for an expansion in powers of $1/Z$; one obtains

$$q = \left[\frac{2}{3\pi}(15\pi Z)^{1/3} + (20\gamma/9\pi^2) + ... \right] \frac{me^2}{\hbar^2} \ , \tag{29}$$

the correction being caused by the q^6-term in the kinetic energy. One can see that the screening wavevector is slightly larger for a positive ion, in comparison with the neutral atom, *i.e.* the electrons are bound a bit closer to the nucleus in the ion. The corresponding minimum value of the energy is given by

$$E_b = -\frac{3}{4\pi}Z^2(15\pi Z)^{1/3} - (5\gamma/\pi^2)Z^2 + ...\text{ry} \ ; \tag{30}$$

making use of $\beta \simeq 2$ one gets $\gamma \simeq 0.08$ and the binding energy of the ion becomes

$$E_b = -11.7Z^{7/3} - 0.56Z^2 + ...\text{eV} \ . \tag{31}$$

The correction $\delta E_b = -0.56Z^2\text{eV}$ to the binding energy of the positive ion, in comparison with the neutral atom, is small, and it represents the relaxation energy after ionization. Within the Thomas-Fermi model one may obtain an approximate representation for the ionization potential as $I = e\varphi_0 = e^2q/R \simeq 21Z^{1/3}/(\ln Z + \beta + 1/2)\text{eV}$; this represents the mechanical work needed for extracting an electron from the atom. This ionization potential is a slowly varying function

of Z, of the order of 12eV, in qualitative agreement with the empirical data. The relaxation energy, which formally should contribute to the ionization potential, is counter-balanced by the radiation energy associated with the electron motion during the ionization process, so that the above formula for the ionization potential may be taken as a satisfactory approximation. The Thomas-Fermi model offers also the opportunity of estimating the lowest electronic energy levels of an atom; indeed, one electron moves, in this case, in the Coulomb potential of the ion, and one may take the hydrogen-like values given by $-13.6/n^2$eV for its energy levels; for $n = 1$ this value is usually below the ionization potential (though not so for some large Z), but for $n \geq 2$ the energy levels are given by $e\varphi_0 - 13.6/n^2$eV; it may be estimated that the first excited energy level lies somewhere around 3eV, as an average, above the ground-state energy.

For a negative ion of charge $-e$ one may take the potential φ as being given by $\varphi = \varphi_0 - z^*e/r + [(Z + z^*)e/r]e^{-qr}$ for $r < R_1$, and $\varphi = -e/r$ for $r > R_1$, where z^* is a charge to be determined; the Poisson's equation is satisfied, and the electrons are confined to a sphere of radius R_1. The continuity conditions give

$$(Z + z^*)(1 + qR_1)e^{-qR_1} = z^* - 1 \tag{32}$$

and

$$\varphi_0 = eq\frac{z^* - 1}{1 + qR_1} \ ; \tag{33}$$

one can see that z^* must be greater than unity, and φ_0 has positive values. The potential energy $-e\varphi$ has, therefore, a maximum value, and the electrons must tunnel through this potential barrier in order to escape from the negative ion; consequently, the electron affinity is $e\varphi_0$. The electrons, however, according to the quasi-classical approximation, are confined to the sphere of radius R_2, where R_2 is obtained from $\varphi = \varphi_0$ as $qR_2 = \ln(1 + z^*/Z)$. The charge z^* must be confined between the spheres of radius R_1 and R_2, as anti-bound states (damped states), according to the form of the potential φ, and, under this circumstance, the quasi-classical approximation requires small values of φ_0, *i.e.* z^* slightly above unity; in this case qR_1 acquires large values, and the potential barrier is very flat. Since the electron density is $n = (1/4\pi e)q^2(\varphi - \varphi_0)$, within the potential barrier we have a density of the order of $n = (1/4\pi e)q^2\varphi_0$; the charge z^* is therefore obtained as $z^* = (1/4\pi e)q^2\varphi_0(4\pi R_1^3/3)$, and using (33), one gets $z^* = 1 + 3/(qR_1)^2$. Equation (32) becomes approximately $Z = 3e^x/x^3 - 1$, for $x = qR_1$, and the solution can again be represented as $qR_1 \simeq \ln Z + \beta$, where β increases slowly with Z around $\beta = 5$. The electron affinity A is therefore given by $e\varphi_0 \simeq 3e^2q/x^3$, and, using the same q as for a neutral atom (which is a good approximation), one gets $A = 63Z^{1/3}/(\ln Z + \beta)^3$eV for the electron affinity; this quantity varies slowly with Z, and has a typical value 0.3eV, which agrees qualitatively with the empirical data.

Let us note that the Poisson's equation can be solved both for positive and negative ions, under appropriate boundary conditions, so that there is no need anymore of introducing the charge-separation radius R_1; this sort of more accurate computations, however, lead to results which are close to the estimations made above. In this respect, the quasi-classical approximation may be used for the motion inside the potential barrier, with a negative kinetic energy and a negative density, within the linear approximation (providing the potential is smooth enough). It is worth noting, however, that the quasi-classical approximation is inaccurate at large distances, so that the above results concerning the ions should be taken only as a qualitative estimation. In addition, we note that for short distances the quantum corrections are important, and in the case of a negative ion these corrections may lead to quasi-bound electron states within the potential well, with positive energies; in this circumstance we get a negative electron affinity. In general, Schrodinger's equation for one-particle wavefunctions can be considered, for the motion in the self-consistent

electric potential (satisfying the Poisson's equation), and this amounts obviously to the density-functional approach; which, in the present case would be a linearized density-functional theory.

Let us consider an atomic cluster with a nuclear charge distribution $e\rho(\mathbf{r})$, where

$$\rho(\mathbf{r}) = \sum_i z_i \delta(\mathbf{r} - \mathbf{r}_i) \quad ; \tag{34}$$

the Poisson's equation reads

$$\Delta\varphi = -4\pi e\rho(\mathbf{r}) + 4\pi en(\mathbf{r}) \quad , \tag{35}$$

and the linear approximation

$$\frac{\hbar^2 k_F}{2m}\delta k_F - e\varphi = -e\varphi_0 \tag{36}$$

is used for the quasi-classical description; the electron density is therefore given by

$$n(\mathbf{r}) = \frac{1}{3\pi^2}k_F^2 \delta k_F = \frac{1}{4\pi e}q^2(\varphi - \varphi_0) \quad , \tag{37}$$

where

$$q^2 = \frac{8me^2 k_F}{3\pi\hbar^2} \quad . \tag{38}$$

In principle, k_F depends on orientation too, as for an anisotropic Fermi surface, but the effects of this anisotropy are small for large clusters, and they will be neglected here; in addition we take $\varphi_0 = 0$, as for a neutral cluster. We solve equation (35) for the Fourier transform $\varphi(\mathbf{k})$ of the potential, by using

$$\rho(\mathbf{r}) = \sum_i z_i \delta(\mathbf{r} - \mathbf{r}_i) = \frac{1}{(2\pi)^3}\int d\mathbf{k}\cdot\rho(\mathbf{k})e^{i\mathbf{k}\mathbf{r}} \quad , \tag{39}$$

where

$$\rho(\mathbf{k}) = \sum_i z_i e^{-i\mathbf{k}\mathbf{r}_i} \tag{40}$$

is the structure factor of the cluster. The field potential is easily obtained as

$$\varphi(\mathbf{r}) = \frac{4\pi e}{(2\pi)^3}\int d\mathbf{k}\cdot\frac{\rho(\mathbf{k})}{k^2+q^2}e^{i\mathbf{k}\mathbf{r}} \quad , \tag{41}$$

and, according to the linear approximation, the kinetic energy is given by

$$E_{kin} = \frac{\hbar^2 k_F^4}{10\pi^2 m}\int d\mathbf{r}\cdot\delta k_F = \frac{4}{5\pi}\left(\frac{3\pi\hbar^2}{8me^2}\right)^3 Ze^2 q^4 \quad , \tag{42}$$

where $Z = \sum_i z_i$ is the total charge-number of the cluster. The potential energy of the electrons can be written as

$$E_{pot}^e = \int d\mathbf{r}\cdot\left(\rho_e\varphi - \frac{1}{2}\rho_e\varphi_e\right) = \frac{1}{2}\int d\mathbf{r}\cdot(\rho_e\varphi + \rho_e\varphi_c) \quad , \tag{43}$$

where $\rho_e = -en$ is the electronic charge density and

$$\varphi_c = e\int d\mathbf{r}'\cdot\frac{\rho(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} = \frac{4\pi e}{(2\pi)^3}\int d\mathbf{k}\cdot\frac{\rho(\mathbf{k})}{k^2}e^{i\mathbf{k}\mathbf{r}} \tag{44}$$

is the (core) field produced by the nuclei; the potential energy becomes

$$E_{pot}^e = -\frac{2\pi e^2 q^2}{(2\pi)^3} \int d\mathbf{k} \cdot \frac{\rho(\mathbf{k})\rho(-\mathbf{k})}{k^2 + q^2} \left(\frac{1}{k^2 + q^2} + \frac{1}{k^2} \right) \quad . \tag{45}$$

The potential energy E_c of the nuclei must be added to the above electron energy; it is given by

$$E_c = \frac{e}{2} \int d\mathbf{r} \cdot \rho \varphi_c = \frac{2\pi e^2}{(2\pi)^3} \int d\mathbf{k} \cdot \frac{\rho(\mathbf{k})\rho(-\mathbf{k})}{k^2} \quad . \tag{46}$$

We assume a typical cluster model with a central charge z_0 and the remaining $z_s = Z - z_0$ charges distributed symmetrically over a spherical surface of radius R; it may be called a shell-cluster model;[2] as a first approximation we shall distribute the shell charge z_s continuously and uniformly over the cluster shell; the structure factor for this model is

$$\rho(\mathbf{k}) = z_0 + z_s \frac{\sin kR}{kR} \quad , \tag{47}$$

corresponding to a nuclear charge distribution

$$\rho(\mathbf{r}) = z_0 \delta(\mathbf{r}) + \frac{z_s}{4\pi R^2} \delta(r - R) \quad . \tag{48}$$

Making use of this structure factor one gets easily the field potential

$$\varphi(\mathbf{r}) = e \left(z_0 + z_s \sinh qR/qR \right) \frac{e^{-qr}}{r} \quad , \quad for \ r > R \quad ,$$

$$\varphi(\mathbf{r}) = \frac{e}{r} \left(z_0 e^{-qr} + \frac{z_s}{qR} e^{-qR} \sinh qr \right) \quad , \quad for \ r < R \quad , \tag{49}$$

and the (core) potential of the nuclear distribution

$$\varphi_c(\mathbf{r}) = eZ/r \quad , \quad for \ r > R \quad ,$$

$$\varphi_c(\mathbf{r}) = ez_0/r + ez_s/R \quad , \quad for \ r < R \quad . \tag{50}$$

(One can check that the jump in the electric field $\mathbf{E} = -grad\varphi$ at the cluster surface is z_s, as it should be; as well as for the electric field $\mathbf{E}_c = -grad\varphi_c$ of the nuclear charges). Now, by direct $\mathbf{r}$-integration one obtains the energies

$$E_{pot}^e = -\frac{e^2 q}{4} [3z_0^2 + \frac{2z_0 z_s}{x}(2 - 2e^{-x} + xe^{-x}) +$$

$$+ \frac{z_s^2}{2x^2}(-1 - 2xe^{-2x} + e^{-2x} + 4x)] \quad , \tag{51}$$

where $x = qR$, and

$$E_c = \frac{e^2 q}{2}(Z^2 - z_0^2)\frac{1}{x} \quad , \tag{52}$$

so that the total potential energy reads

$$E_{pot} = -\frac{e^2 q}{4} \left[3z_0^2 + \frac{2z_0 z_s}{x}(x - 2)e^{-x} + \frac{z_s^2}{2x^2}(-1 - 2xe^{-2x} + e^{-2x}) \right] \quad . \tag{53}$$

This potential energy decreases monotonically with increasing x, indicating that the continuous

shell-cluster model is unstable; as it is known, the Thomas-Fermi model with a spatially extended nuclear charge is indeed unstable.[3] In general, the stability arises from the quantal behaviour, Fermi statistics included, for a discrete atomic structure; the latter is essential for a cluster-shell of large size. Consequently, it is safe to use the above potential energy for small x, *i.e.*

$$E^s_{pot} = -\frac{e^2 q}{4}\left[3Z^2 - 2\frac{Z^2 - z_0^2}{x} + ...\right] \ , \ \ for \ \ x \sim 0 \ \ , \tag{54}$$

while the cluster should be viewed as a collection of neutral atoms for large values of x; consequently, one may use as a reasonable approximation the potential energy E_{pot} obtained above, out of which the potential energy of the nuclear charges E_c is subtracted; this amounts to E^e_{pot} given by (51) for large x, *i.e.*

$$E^l_{pot} = -\frac{e^2 q}{4}\left[3z_0^2 + 2\frac{Z^2 - z_0^2}{x} + ...\right] \ , \ \ for \ \ x \sim \infty \ \ ; \tag{55}$$

indeed, for moderate values of x the potential energy given by (55) is of the same order $\sim e^2 q Z^2$ as the potential energy given by (54), while only at large distances it overestimates the energy of a collection of N neutral atoms; indeed, a collection of N neutral atoms, each of atomic number z^*, such that $Z = Nz^*$, has a Thomas-Fermi potential energy of the order $\sim -e^2 q N z^{*2}$, according to the above computations, while the energy given by (55) is of the order $\sim -e^2 q z^{*2}$ for large x; therefore, as long as the equilibrium is reached for a moderate distance x the two asymptotic potential energies given above can be used as a good approximation. By taking into account the discrete atomic strucure of the cluster the $1/x$-contributions in (54) and (55) will be slightly modified, as well as the behaviour of the energy at moderate values of x. For a qualitative estimation any reasonable interpolation between these two asymptotic potential energies may be employed; we choose

$$\begin{aligned} E_{pot} &= [E^s_{pot} - E^l_{pot}]e^{-x} + E^l_{pot} = \\ &= -\frac{e^2 q}{4}\left[3z_0^2 + (Z^2 - z_0^2)\left(3e^{-x} + 2\frac{1 - 2e^{-x}}{x}\right)\right] \ . \end{aligned} \tag{56}$$

This energy has indeed a minimum value $E_{pot} = -0.41e^2 q Z^2(1+0.8\alpha)$ for $x \simeq 1$, where $\alpha = z_0^2/Z^2$; a more accurate computation for a discrete distribution of nuclear charges will give, however, a greater value for the parameter x at equilibrium, and a higher potential energy.

Adding now the kinetic energy given by (42), and minimizing with respect of q, one obtains

$$q = \frac{2}{3\pi}(8.2\pi)^{1/3}Z^{1/3}(1 + 0.27\alpha)(1/a_H) = 0.63Z^{1/3}(1 + 0.27\alpha)(1/a_H) \ \ , \tag{57}$$

and the binding energy of the cluster

$$E_b = -0.31Z^2 e^2(1 + 0.8\alpha)q = -5.31Z^{7/3}(1 + \alpha)\text{eV} \ \ ; \tag{58}$$

or, in view of the discussion made above about the correcting kinetic energy and the virial theorem, a more accurate value is probably $E'_b = (4/3)E_b = -7.08Z^{7/3}(1 + \alpha)\text{eV}$. From $x \simeq 1$ obtained above one gets the radius of the cluster at equilibrium

$$R \simeq 1/q = 1.6Z^{-1/3}(1 - 0.27\alpha)(a_H) \ . \tag{59}$$

The expansion of the potential energy around the minimum value gives $E''_{pot}(x \simeq 1) = 0.56e^2 Z^2 q(1-\alpha)$, which leads to a typical frequency ω of the radial vibrations of the cluster as given by

$$\hbar\omega = 10Z^{3/2}(1 - 0.1\alpha)\sqrt{m/M_s}\text{eV} \quad , \tag{60}$$

where M_s is the mass of the cluster shell.

Let us apply the above computations to a particular cluster $Fe_{13}(C_2H_2)_6$, which is claimed to have been prepared recently;[4] very likely, this cluster has an icosahedral structure, and the ethylene radical C_2H_2 behaves like an autonomous atomic entity. In general, the formation of such chemical objects does not involve all the electrons, but only a small fraction; therefore, we assume a generic structure of N atomic constituents, each of them with an effective charge z^*; for the present case we take $N = 13$. The "binding energy" of the cluster is in fact its formation enthalpy, which, by using (18) and (58), can be written as

$$E \simeq N(5.31N^{4/3} - 11.7)z^{*7/3}\text{eV} \quad ; \tag{61}$$

for typical values of this energy of the order of $10^2 - 10^3$eV, as obtained from "*quantum ab initio*" computations, the effective charge in (61) is $z^* \sim 0.2 - 0.75$, which is in agreement with similar estimations based on such computations (however, the validity of the Thomas-Fermi model for such small values of the charge number is questionable; for a discrete distribution of nuclear charges the effective charge z^* increases, very likely toward $z^* \sim 1$); the radius of the cluster, as given by (59), is

$$R \simeq 1.6z^{*-1/3}N^{-1/3}(a_H) \quad , \tag{62}$$

which yields $R \simeq 1$Å, for the above estimations; these values are also in agreement with those obtained by other approaches; however, for a more realistic computation, where the discrete atomic structure of the cluster is included, the values of the cluster radius will be larger; the characteristic infrared frequency of radial vibrations as given by (60) is estimated at $\sim 20 - 200$meV, *i.e.* $\sim 160 - 1600$cm^{-1}, which is again in qualitative agreement with other estimations, and with the experimental data.[5]

We note that from the above computations one can also obtain easily the change δE in the cluster energy under deformations, *i.e.* for a variation δS of the area of its surface for a constant volume; indeed, the cluster radius changes by $\delta R \sim \delta S/R$ in this case, and $\delta R \sim R\delta q/q$ from the equilibrium condition found above; hence, from $\delta E \sim (\delta q)^2$ around the equilibrium position, one obtains readily the desired dependence $\delta E \sim (\delta S)^2$. We note also that such clusters may also be viewed approximately as atoms with a total effective charge Nz^*, where N is the number of atoms in the cluster; under these circumstances one may use the formulae obtained above for the ionization potential $I \sim 21(Nz^*)^{1/3}/[\ln(Nz^*) + \beta + 1/2]$ eV and electron affinity $A \sim 63(Nz^*)^{1/3}/[\ln(Nz^*) + \beta]^3$ eV; for the particular cluster mentioned above with $N = 13$ and $z^* \sim 1$ one gets the ionization potential $I \sim 10$eV and the electron affinity $A \sim 0.3$eV; the lowest-energy electronic states can also be estimated in this case, by comparing the ionization potential with the hydrogen-like energy levels. Another interesting point would be that of adopting a different structure for the nuclear charge distribution in the above computations, for instance a uniformly distributed charge within a sphere, *i.e.* a filled sphere, instead of a surface distribution; this model would be more appropriate for much larger clusters, and may serve as a model calculations for the surface energy. Of course, various geometric structures can also be considered in estimating the structure factor, in order to get the most stable one. The results of such computations should be compared with the non-linear Fermi model, in order to get an estimate of the quantal effects, as discussed above, and first-order contributions within the perturbation theory must be included.

In addition, the occurence of electron states with high orbital momenta l can be estimated for a cluster, in a similar manner as for an atom; using the electron potential φ as given by (49) for $r > R$, for instance, one obtains $Z \simeq 0.03(2l + 1)^3$, which indicates that the atomic shell-model for clusters with small effective charges z^* ($Z = Nz^*$) is not appropriate (for large Z and l the model is irrelevant; except for the shell-effects of state-bunches, as arising from finite motion and potential symmetries; which, however, are not very effective in the case of the shell-cluster model); indeed, the binding electrons move mainly around the nuclear shell in this case, and their orbital momenta are relatively high.

Speaking of the orbital momentum of the electrons it is worth noting an interesting point regarding the spin of the shell-cluster model described above. As it is well known, the spin-orbit interaction is proportional to the derivative of the potential φ, and, since this derivative has opposite signs across the cluster surface, one may infere that the electron spins have also opposite orientations across this surface, in order to take advantage of this energy. Consequently, the cluster possesses a total, non-vanishing spin S, proportional to the jump in the electron density across the cluster surface,

$$S = \frac{1}{2}(4\pi) \int dr \cdot r^2 n_+ - \frac{1}{2}(4\pi) \int dr \cdot r^2 n_- \quad, \tag{63}$$

where $n_\pm$ are the electron densities in the two regions separated by the cluster surface; one may also write

$$S = 2\pi R^2 \left(\int dr \cdot n_+ - \int dr \cdot n_- \right) = 2\pi R^3 \Delta(\partial n/\partial r)\delta R \quad, \tag{64}$$

where the integration is restricted to a small range δR across the surface (over which the derivative of the potential falls abruptly), and $\Delta(\partial n/\partial r)$ is the jump of the density derivative across this surface (we neglect the cluster central region, which contributes less); now, since $n = (q^2/4\pi e)\varphi$, we have $\Delta(\partial n/\partial r) = (q^2/4\pi e)\Delta\mathcal{E}$, where $\mathcal{E}$ denotes the electric field across the surface, and one obtains therefore $\Delta(\partial n/\partial r) = q^2 z_s/4\pi R^2 \simeq q^2 Z/4\pi R^2$. The cluster spin is consequently obtained from (64) as $S \simeq (1/2)Rq^2 Z\delta R$, and taking $\delta R \sim 1/q$ as the range over which the density falls most abruptly, one gets $S \sim (1/2)qRZ \sim (1/2)Z$; for a cluster with N atomic constituents and an atomic effective charge z^* we may estimate the spin as given by $S \sim Nz^*/2$; for the particular cluster $Fe_{13}(C_2H_2)_6$ discussed above ($N = 13$, $z^* \simeq 1$) one obtains $S \sim 6.5$, and therefore a magnetic moment $\mu \sim 13\mu_B$, where μ_B is the Bohr magneton. Consequently, the cluster is paramagnetic; in addition, there exists also a small cluster diamagnetism. Indeed, as it is known, the electrons in a uniform magnetic field $\mathbf{H}$ have a diamagnetic energy

$$\delta E = -\frac{e^2}{8mc^2} \sum_i \overline{(\mathbf{H} \times \mathbf{r}_i)^2} \quad, \tag{65}$$

where the summation extends over all the electrons (and c denotes the light velocity); from the above equation one obtains easily

$$\delta E = -\frac{e^2 H^2}{12mc^2} \sum_i \overline{r_i^2} = -\frac{e^2 H^2}{12mc^2} \int d\mathbf{r} \cdot r^2 n(\mathbf{r}) \quad, \tag{66}$$

where $n(\mathbf{r}) = q^2\varphi(\mathbf{r})/4\pi e$ is the electron density, the field potential $\varphi(\mathbf{r})$ being given by (49). The computations in the equation above are straightforward, and one gets

$$\delta E = -\frac{7e^2 Z H^2}{12mc^2 q^2}(1 - \sqrt{\alpha}/7) = -1.47 Z^{1/3}(e^2 H^2/mc^2)(1 - 0.14\sqrt{\alpha})(a_H)^2 \quad; \tag{67}$$

the atomic cluster has therefore a small diamagnetic susceptibility

$$\chi_d = -2.94 Z^{1/3}(e^2/mc^2)(1 - 0.14\sqrt{\alpha})(a_H)^2 =$$

$$= -1.57 Z^{1/3}(1 - 0.14\sqrt{\alpha}) \cdot 10^{-4}(a_H)^3 \quad . \tag{68}$$

There is another point worth mentioning, namely the cluster electric polarizability. An external, uniform electric field $\mathbf{E}$ produces a potential $\Phi = -\mathbf{Er}$ and a small perturbation $\delta n \sim \mathbf{Er}$ in the electron density (the nuclear charge distribution is practically not affected); one can see that $\int d\mathbf{r} \cdot \delta n = 0$, and the kinetic energy does not change; the variation of the potential energy must compensate the external field energy, *i.e.*

$$-\frac{2\pi e^2}{q^2} 2n\delta n - \frac{1}{2} e\varphi_c \delta n + en\mathbf{Er} = 0 \quad , \tag{69}$$

where use has been made of $n = q^2\varphi/4\pi e$; hence,

$$\delta n = \frac{q^2}{4\pi e} \frac{\varphi}{\varphi + \varphi_c/2} \mathbf{Er} \quad , \tag{70}$$

so that the change in the energy is given by

$$\delta E = -\frac{2\pi e^2}{q^2} \int d\mathbf{r} \cdot (\delta n)^2 = -\frac{q^2}{8\pi} \int d\mathbf{r} \cdot \frac{\varphi^2}{(\varphi + \varphi_c/2)^2}(\mathbf{Er})^2 \quad ; \tag{71}$$

for an atom, one may neglect φ in the denominator above in comparison with φ_c, and obtains $\delta E = -\mathcal{E}^2/2q^3$; hence, the atomic polarizability $\chi_e = 1/q^3 \simeq 2.2Z^{-1}(a_H)^3$, *i.e.* the well known qualitative result $\chi_e \sim R^3$, where R is the "radius" of the atom. A similar calculation for the shell-cluster model gives $\chi_e \simeq 1/3q^3 \simeq 1.33Z^{-1}$ for the electric polarizability of the cluster; (in general, however, one should note that the r^n-integrals are overestimated by the Thomas-Fermi model).

Finally, it is worth noting that the present method can be extended to finite temperatures, in order to get the equation of state for clusters.[5]

References

[1] L. H. Thomas, Proc. Cambr. Phil. Soc. **23** 542 (1927); E. Fermi, Z. Physik **48** 73 (1928).

[2] N. H. March, Proc. Cambr. Phil. Soc. **48** 665 (1952).

[3] E. Teller, Revs. Mod. Phys. **34** 627 (1962).

[4] I. Morjan, F. Huisken et al, private communication.

[5] For reviews on atomic clusters see M. Brack, Revs. Mod. Phys. **65** 677 (1993), and W.A. de Heer, *ibid* 611

[6] R. Feynman, N. Metropolis and E. Teller, Phys. Rev. **75** 1561 (1949).