

On the self-consistent field of the atoms and Hartree's equations

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Abstract

The variational approach to the linear Thomas-Fermi model is explained again, and the general principles of the atomic theory are briefly outlined.

In the non-relativist limit of small velocities one may consider the electrons in an atom as moving in the Coulomb field of the atomic nucleus and interacting with one another by the Coulomb force; the relativist interactions involve both spin-orbit and spin-spin couplings, and their main correction to the energy is of the order of v^2/c^2 , where v is the electron velocity and c is the light velocity; the electron energies in a Coulomb field of a point-charge Ze , where Z is the atomic number and $-e$ is the electron charge, are given by the hydrogen-like energy levels[1] $E_n = -Z^2/2n^2$, in atomic units, where $n = 1, 2, \dots$ is the (principal) quantum number (and the center-of-mass effects are neglected); the atomic unit for energy is $e^2/a_H = 2\text{ry} \simeq 27.2\text{eV}$ (*i.e.* twice the rydberg ry), and $a_H = \hbar^2/me^2 \simeq 0.53\text{\AA}$ is the Bohr radius; here, \hbar is Planck's constant and m is the electron mass; according to the virial theorem the (average) kinetic energy T and the (average) potential energy U in the Coulomb field are related by $2T = -U$, so that the lowest-energy state of an electron in a hydrogen-like atom has a kinetic energy of the order of 100keV for $Z \sim 100$, for instance; such an energy has to be compared with the electron rest energy $mc^2 \sim 500\text{keV}$; one may see that the non-relativist limit is appropriate for atoms, except for stronger-bound electron states for large Z ; though they do contribute significantly to the atom energy, such states (which are called also inner states) are a few for large Z , so that, under this circumstance, one may neglect, to the first approximation, the relativist interactions between the electrons in atoms (as we may neglect also the relativist hyperfine interaction between the electrons spins and the nuclear spins); the atom conserves its (total) orbital momentum L in this case, as for the motion in a central external field (plus interaction), and, likewise, the electrons conserve their total spin S ; where the relativist interactions matter however, only the total angular momentum J is conserved, as for a closed system symmetric under rotations; in the former case the atomic states are classified by the so-called LS -terms scheme (or Russell-Saunders scheme[2]), while in the latter case a J -labeled fine structure of multiplets splits the LS -terms into levels, and a jj -coupling between individual angular momenta j of the electrons is more appropriate.

On the other hand, the electrons in an atom are described, in principle, by a multi-particle wavefunction; since the Coulomb attraction of the nucleus may accomodate many electrons on single-particle states, according to the Pauli exclusion principle,³ a first attempt would be that of treating the Coulomb repulsion between electrons as a small perturbation; however, such an attempt is inadequate, in general, especially for heavy atoms, because at large distances from the nucleus the Coulomb attraction of the latter is cancelled, to a large extent, by the Coulomb

repulsion between the electrons, so that the Coulomb repulsion can not be treated, in general, as a small perturbation, due to its long-range character; this long-range character of the Coulomb force matters for the peripheral, or outer, electron states, which are the majority in heavy atoms; a certain amount of repulsion between the electrons should, therefore, be included, beside the attraction, such as to generate a screened, self-consistent field, wherein the individual electrons move in single-particle states; the screening may ensure a certain "smallness" of the self-consistent field, such as to treat its effects as small perturbations; this "smallness" is the slow spatial variation of the field. One may start, therefore, with a Slater determinant of single-particle states for the electrons in an atom (spin included, called also spin-orbitals),[4] and derive the corresponding Schrodinger equation, both for the ground-state and for the excited states, by requiring the extrema of energy, the orthogonality, and the normalization of the single-particle wavefunctions; one obtains this way the (coupled and non-linear) Hartree-Fock equations,[5] which describe the single-particle states of the electrons moving in a self-consistent field; this field includes both a local direct contribution (the Hartree term) and a non-local (or off-diagonal) exchange contribution (the Fock, or Fock-Dirac term[6]), the latter being more reminiscent of the original interaction. The multi-particle wavefunction is approximated this way by an antisymmetrized sum of products of single-particle wavefunctions, and the validity of this approximation remains to be checked. The validation of this procedure consists in estimating the life-time of the Hartree-Fock single-particle states, as due to the original interaction; in a usual manner, the Hartree-Fock self-consistent field, which is the average of the original (total) interaction over the states we are looking for, is added to the kinetic term and then subtracted from the original interaction, so that the latter contribution is a new interaction, which is called the residual interaction; this residual interaction generates finite life-times to the second-order of the perturbation theory, as the first main contribution; as long as this contribution is sufficiently small to be neglected, one may say that the Hartree-Fock single-particle states are the right states, and, consequently, the many-particle wavefunction of the interacting system is satisfactorily represented by single-particle wavefunctions, to this extent; as known, the transition probabilities between single-particles states are controlled by the corresponding matrix elements of the interaction, as compared with the energy gaps, and the associated finite life-times are due to the scattering processes described by these matrix elements;[7] consequently, as long as the self-consistent field is small, *i.e.* varies slowly in space, the transition probabilities are small enough to be neglected, and the single-particle states of the self-consistent field are valid; this perturbational procedure for the residual interaction stops therefore to the first-order, in the sense that the first-order contribution to energy vanishes, and the first-order contributions to the Hartree-Fock single-particle states are irrelevant, as generating second-order contributions to energy, *i.e.* contributions of the same order as those corresponding to finite life-times; in this sense, the question of the "convergence" of the perturbation series is both irrelevant and useless. In the particular case of the electron states in an atom the self-consistent field is small, almost vanishing, over large distances, due to the electrons screening; the Hartree-Fock procedure is therefore valid, to this extent; the abrupt variation of the self-consistent field near the nucleus does not contribute much, as it extends over a small region; comparatively, it may affect more the inner electron states, and, in this respect, a genuine multi-particle wavefunction might be more adequate for them; for the rest of the outer states, however, the single-particle approximation is valid, in the sense discussed here. In addition, in view of its non-local character, the exchange contribution is more effective for the inner electron states, whose spatial variations are smoother, but it becomes gradually irrelevant for the outer single-particle states.

In the self-consistent field the single-particle states of the electrons in an atom occur in energy shells, or bunches, according to the symmetries, and the form, of the field; to a first approximation they may conventionally be labelled by a principal quantum number n and an orbital (or angular)

quantum number l , both integers, as for a hydrogen-like atom, or a central field, and the filling up of the states proceeds by various nl -configurations, or shells; [8] for any integer n the orbital number takes the values $l = 0, 1, \dots, n-1$, with $2(2l+1)$ states for every l , the factor 2 accounting for the two spin orientations; for a closed shell the self-consistent field is central (due to the closure, or completeness, of the spherical harmonics), [9] and the term of the atom is always 1S , *i.e.* the spin is zero ($2S+1 = 1$) and the orbital momentum is zero ($L = 0$); accidentally, the n -energy levels in the Coulomb field are fully degenerated for all l -values, and part of this degeneracy is approximately preserved in the closed nl -configurations too; the atomic terms are computed, in general, by adding the angular momenta and, separately, the spins, but for electron states in the same configuration, like, for instance, in an open shell, these additions are restricted by the Pauli exclusion principle; in this case, the possible terms are found by adding the magnetic numbers (projections of l) and by adding the spins of the electrons; for an incomplete shell a mixture of Slater determinants is needed in general (which is sometimes extended to mixing up the configurations), *i.e.* the orbital momenta are, in general, coupled, by interaction, to one another; in an open, or incomplete, shell the electrons try to minimize their Coulomb repulsion, so that their total spin tends to have a maximum value (as for an as antisymmetric as possible spatial orbital); on the other hand, their total angular momentum L tends also to have a maximum value; these are Hund's semi-empirical rules, [10] and they hold both for the first half of electrons and for the second half of electron holes in an open shell; the energy levels change with increasing Z , and this variation combines with the filling up of the shells to produce the small, irregular, quasi-periodic variations of some of the atomic properties, like the ionization potentials, for instance; in addition, the nl -configurations exhibit inversions in their energies, such that intermediate periods of elements intervene, and are accommodated inside the main periods in the periodic table of elements; for instance, the energy order is approximately $\dots 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, \dots$ etc, where s, p, d, f, g, \dots are used for $l = 0, 1, 2, 3, 4, \dots$, and several inversions occur also inside this series. The first main period in the table of elements starts with H($1s^1$) and ends with He($1s^2$); it follows Li($1s^2 2s^1$), Be($1s^2 2s^2$), and B($1s^2 2s^2 2p^1$) up to Ne($1s^2 2s^2 2p^6$); the next series is Na($\dots 3s^1$), Mg($\dots 3s^2$) and Al($\dots 3s^2 3p^1$) up to Ar($\dots 3s^2 3p^6$); now, it appears the first inversion K($\dots 4s^1$), Ca($\dots 4s^2$) followed by Sc($\dots 4s^2 3d^1$)...V($\dots 4s^2 3d^3$), Cr($\dots 4s^1 3d^5$), Mn($\dots 4s^2 3d^5$)...Ni($\dots 4s^2 3d^8$), Cu($\dots 4s^1 3d^{10}$), Zn($\dots 4s^2 3d^{10}$); this is known as the Fe-group (or series), and it is worth noting for the two sd -inversions, or competitions, corresponding to Cr and Cu; it follows Ga($\dots 4s^2 3d^{10} 4p^1$) up to Kr($\dots 4s^2 3d^{10} 4p^6$); then it appears another inversion Rb($\dots 5s^1$), Sr($\dots 5s^2$), then the group of Pd with several sd -inversions: Y($\dots 5s^2 4d^1$), Zr($\dots 5s^2 4d^2$), Nb($\dots 5s^1 4d^4$)...Rh($\dots 5s^1 4d^8$), Pd($\dots 4d^{10}$), Ag($\dots 5s^1 4d^{10}$), Cd($\dots 5s^2 4d^{10}$); followed by In($\dots 5s^2 4d^{10} 5p^1$)...Xe($\dots 5s^2 4d^{10} 5p^6$); here, another inversion Cs($\dots 6s^1$), Ba($\dots 6s^2$), then La($\dots 6s^2 5d^1$), and now it follows the rare earths Ce($\dots 6s^2 4f^2$)...Eu($\dots 6s^2 4f^7$), Gd($\dots 6s^2 5d^1 4f^7$), Tb($\dots 6s^2 4f^9$)...Yb($\dots 6s^2 4f^{14}$), Lu($\dots 6s^2 5d^1 4f^{14}$) with a df -competition; the group of Pt continues with Hf($\dots 6s^2 5d^2 4f^{14}$)...Ir($\dots 6s^2 5d^7 4f^{14}$), Pt($\dots 6s^1 5d^9 4f^{14}$), Au($\dots 6s^1 5d^{10} 4f^{14}$), Hg($\dots 6s^2 5d^{10} 4f^{14}$); followed by Tl($\dots 6s^2 5d^{10} 4f^{14} 6p^1$)...Rn($\dots 6s^2 5d^{10} 4f^{14} 6p^6$); finally, it follows Fr($\dots 7s^1$), Ra($\dots 7s^2$), then Ac($\dots 7s^2 6d^1$) and the actinides Th($\dots 7s^2 6d^2$), Pa($\dots 7s^2 6d^1 5f^2$)...Np($\dots 7s^2 6d^1 5f^4$), Pu($\dots 7s^2 5f^6$)...Cm($\dots 7s^2 6d^1 5f^7$), Bk($\dots 7s^2 6d^1 5f^8$), Cf($\dots 7s^2 5f^{10}$)...No($\dots 7s^2 5f^{14}$), Lr($\dots 7s^2 6d^1 5f^{14}$), Ku($\dots 7s^2 6d^2 5f^{14}$); etc; similar inversions occur for ions, as, for instance, $V^+(\dots 3d^4)$ (and not $(\dots 4s^1 3d^3)$ or $(\dots 4s^2 3d^2)$); etc.

For large Z the most part of the electrons in single-particle states are located at intermediate distances from the nucleus; the self-consistent field varies slowly over such distances, and it accommodates many electrons, so that these electrons admit a quasi-classical (and statistical) description. [11] Within such a description the electron states are described by quasi-plane waves, and the Fermi sea is filled up to a certain quasi-Fermi momentum, which has a spatial variation, according to the self-consistent field; the quasi-classical description is valid as long as the

electron wavelength has a slow spatial variation, *i.e.* the variation of the potential energy over a distance of the order of the wavelength is small in comparison with the kinetic energy; therefore, the quasi-classical description holds for distances longer than the radius a_H/Z of the first Bohr orbit, where the quantum corrections become important, and shorter than the Bohr radius a_H , where the wavelengths get longer and longer (this is the meaning of "intermediate" distances); the quasi-classical description holds therefore for large Z . The quasi-classical motion of the electrons proceeds by conserving the local classical energy of the Fermi level

$$\hbar^2 k_F^2 / 2m - e\varphi = 0 \quad , \quad (1)$$

where k_F is the Fermi momentum and φ is the self-consistent field; the total energy at infinite vanishes, as for a neutral atom. This equation is invalid near the atomic nucleus, where the field varies abruptly, and quantum corrections are needed for those regions; the main source of error in this case is the replacement of the quantum kinetic energy by its classical form; on the other hand, over those intermediate regions, where the quasi-classical description holds, and the self-consistent field varies slowly, one may employ a linearized form of the kinetic energy by replacing k_F^2 by $k_F \delta k_F$, where k_F is regarded as a parameter constant in space, and the whole spatial dependence is transferred upon δk_F ; over these regions k_F is indeed comparable with δk_F , and such a linearized form of the kinetic energy is appropriate; however, in doing so, the abrupt variation of the self-consistent field in the vicinity of the nucleus is neglected, and the results must be corrected by the corresponding contribution of the potential energy; this may be done by using the first-order perturbation theory for the self-consistent field φ over a certain small region around the nucleus; this correction is made shortly below. Going further on with this approach, the electron density $n = k_F^3 / 3\pi^2$ is written as $n = k_F^2 \delta k_F / 3\pi^2$, such that, by using (1), one obtains

$$n = (2mek_F / 3\pi^2 \hbar^2) \varphi = (q^2 / 4\pi e) \varphi \quad , \quad (2)$$

where

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

is a parameter to be determined variationally; the self-consistency is ensured through Poisson's equation

$$\Delta\varphi = -4\pi e Z \delta(\mathbf{r}) + 4\pi e n = -4\pi e Z \delta(\mathbf{r}) + q^2 \varphi \quad , \quad (4)$$

whose solution is the screened field

$$\varphi = \frac{Ze}{r} e^{-qr} \quad , \quad (5)$$

and the corresponding electron density is

$$n = q^2 \frac{Z}{4\pi r} e^{-qr} \quad ; \quad (6)$$

one obtains this way a linearized version of the Thomas-Fermi model.[12] The kinetic energy $E_{kin} = V \hbar^2 k_F^5 / 10\pi^2 m$ of the Fermi gas is replaced by its linearized version

$$E_{kin} = \frac{\hbar^2 k_F^4}{10\pi^2 m} \int d\mathbf{r} \cdot \delta k_F = \frac{e}{5\pi^2} (3\pi \hbar^2 / 8me^2)^3 q^6 \int d\mathbf{r} \cdot \varphi \quad , \quad (7)$$

while the potential energy is given by

$$\begin{aligned} E_{pot} &= \int d\mathbf{r} \cdot (\rho_e \varphi - \frac{1}{2} \rho_e \varphi_e) = \frac{1}{2} \int d\mathbf{r} \cdot (\rho_e \varphi + \rho_e \varphi_e) = \\ &= -\frac{e}{2} \int d\mathbf{r} \cdot (n\varphi + n\varphi_e) = -\frac{q^2}{8\pi} \int d\mathbf{r} \cdot (\varphi^2 + \varphi\varphi_e) \quad , \end{aligned} \quad (8)$$

where $\rho_e = -en$ is the density of the electrons charge, $\varphi_e = \varphi - \varphi_c$ is that part of the field produced by the electrons, and $\varphi_c = Ze/r$ is the (core) field of the nucleus. The computations are straightforward, and one obtains

$$E_{kin} = \frac{4}{5\pi} Z e^2 (3\pi\hbar^2/8me^2)^3 q^4 \quad , \quad (9)$$

and

$$E_{pot} = -\frac{3}{4} Z^2 e^2 q \quad ; \quad (10)$$

the minimum value of the total energy $E_{kin} + E_{pot}$ is reached for

$$q = \frac{2me^2}{3\pi\hbar^2} (15\pi)^{1/3} Z^{1/3} = \frac{2}{3\pi} (15\pi)^{1/3} Z^{1/3} a_H^{-1} = 0.77 Z^{1/3} a_H^{-1} \quad ; \quad (11)$$

the value of this minimal energy is

$$E = -\frac{9}{16} Z^2 e^2 q = -0.86 Z^{7/3} \text{ry} = -11.78 Z^{7/3} \text{eV} \quad . \quad (12)$$

One can see that the radial density of electrons $\sim r^2 n$ has a maximum value at $R \sim 1/q \sim Z^{-1/3} a_H$, which may be taken as the "radius" of the electrons charge; while the radius of the atom is of the order of a_H , emphasizing again the validity of the quasi-classical description for large Z . The linearization of the basic equations of the quasi-classical description together with the variational approach, as well as the approximate character of the quasi-classical description in general, which removes the distinction between the kinetic energy and the potential energy, imply the breakdown of the virial theorem; indeed, one can check easily that $E_{kin} = -(1/4)E_{pot}$ (instead of $E_{kin} = -(1/2)E_{pot}$); however, the present variational approach to the linearized Thomas-Fermi equations is more appropriate, and the result is closer to the right one, especially when properly corrected.

The correction to this energy can be computed in the following way; if one assumes a (quasi-) plane wave for each electron state then the first-order perturbation theory gives a change

$$-\frac{e}{V} \int_V d\mathbf{r} \cdot \varphi = -3Z e^2 q \cdot \frac{1}{x^3} (1 - e^{-x} - x e^{-x}) \quad , \quad (13)$$

in the energy of each state, where $V = 4\pi R^3/3$ and $x = qR$; the total change in energy ΔE is obtained by multiplying the above result by the total number of electrons in the volume V , which is given by $\int_V d\mathbf{r} \cdot n$; one obtains

$$\Delta E = -3Z^2 e^2 q \cdot \frac{1}{x^3} (1 - e^{-x} - x e^{-x})^2 = \frac{16}{3} E \cdot \frac{1}{x^3} (1 - e^{-x} - x e^{-x})^2 \quad ; \quad (14)$$

the function of x in the above equation has a maximum value 0.073 for $x \simeq 0.75$, which corresponds to $R \simeq Z^{-1/3} a_H$, and yields

$$\Delta E = 0.39 E = -4.56 Z^{7/3} \text{eV} \quad ; \quad (15)$$

which leads to a total energy

$$E = -11.78 Z^{7/3} \text{eV} - 4.56 Z^{7/3} \text{eV} = -16.34 Z^{7/3} \text{eV} \quad ; \quad (16)$$

this is in good agreement with the empirical data, which give $E \simeq -16 Z^{7/3} \text{eV}$ (up to higher-order corrections, of course, including the small, irregular, quasi-periodic variations due to the shell effects).[13] One may note that the non-linear Thomas-Fermi model leads to an energy

$E = -20.8Z^{7/3}\text{eV}$, which has to be corrected for an additional amount of kinetic energy; however, the corrections are more difficult to be made, as the starting point of the non-linear model is not the most appropriate, and convenient. It is also noteworthy that the exchange energy for a Fermi gas[14] $E_{ex} = -(1/4\pi^3)V e^2 k_F^4$, which, according to the linearization prescription, should be written as

$$E_{ex} = -\frac{1}{4\pi^3} e^2 k_F^3 \int d\mathbf{r} \cdot \delta k_F \quad , \quad (17)$$

is of the order of $-4.53Z^{5/3}\text{eV}$, *i.e.* by a factor $Z^{2/3}$ smaller than the Thomas-Fermi contribution; for large Z it may, therefore, be neglected.

A more accurate treatment, beyond the quasi-classical description, implies the Schrodinger equation

$$-\frac{\hbar^2}{2m} \Delta\psi - e\varphi\psi = E\psi \quad (18)$$

instead of (1), where the self-consistent field φ satisfies the Poisson's equation

$$\Delta\varphi = -4\pi e Z \delta(\mathbf{r}) + 4\pi e \sum |\psi|^2 \quad ; \quad (19)$$

these are Hartree's equations for the single-particle states ψ , and the summation in (19) extends over all these states, filled up with electrons; as one can see, the solution depends on the state of the ensemble of electrons, and on Z ; first, we write these equations again in reduced atomic units a_H for distances and e^2/a_H for energy (the potential φ being measured in e/a_H):

$$\begin{aligned} -\frac{1}{2}\Delta\psi - \varphi\psi &= E\psi \quad , \\ \Delta\varphi &= -4\pi Z \delta(\mathbf{r}) + 4\pi \sum |\psi|^2 \quad ; \end{aligned} \quad (20)$$

then, we write the laplacean as

$$\Delta = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) - \frac{1}{r^2} \mathbf{l}^2 = \Delta_r - \frac{1}{r^2} \mathbf{l}^2 \quad , \quad (21)$$

where \mathbf{l} is the orbital momentum, and expand both the field φ and the wavefunctions ψ in spherical harmonics:

$$\varphi = \sqrt{4\pi} \sum_{lm} \varphi_{lm}(r) Y_{lm} \quad , \quad \psi = \sum_{lm} \psi_{lm}(r) Y_{lm} \quad ; \quad (22)$$

using

$$Y_{lm}^* Y_{l'm''} = \sum_{l''m''} C_{mm'}^{l'l''} (l''m'') Y_{l''m''} \quad , \quad (23)$$

where $C_{mm'}^{l'l''} (l''m'')$ are the Clebsch-Gordan coefficients, the Poisson's equation in (20) becomes

$$\begin{aligned} \sqrt{4\pi} \sum_{lm} (\Delta_r - l(l+1)/r^2) \varphi_{lm}(r) Y_{lm} &= -4\pi Z \delta(\mathbf{r}) + \\ + 4\pi \sum_{\substack{l'm'' \\ lm}} \sum_{l''m''} C_{m'm''}^{l'l''} (lm) \psi_{l'm''}^* \psi_{l''m''} Y_{lm} \quad , \end{aligned} \quad (24)$$

or

$$\begin{aligned} \Delta_r \varphi_{00} &= -4\pi Z \delta(\mathbf{r}) + \sum \sum_{lm} |\psi_{lm}|^2 \quad , \\ (\Delta_r - l(l+1)/r^2) \varphi_{lm} &= \\ = \sqrt{4\pi} \sum \sum_{l'm''} \sum_{l''m''} C_{m'm''}^{l'l''} (lm) \psi_{l'm''}^* \psi_{l''m''} \quad , \quad l \neq 0 \quad ; \end{aligned} \quad (25)$$

similarly, the Schrodinger equation becomes

$$\begin{aligned}
 & -\frac{1}{2} \left(\Delta_r - l(l+1)/r^2 \right) \psi_{lm} - \varphi_{00} \psi_{lm} - \\
 & -\sqrt{4\pi} \sum_{l' \neq 0, m', l'', m''} (-1)^{l'+m'} C_{-m' m''}^{l' l''} (lm) \varphi_{l' m'} \psi_{l'' m''} = \\
 & = E \psi_{lm} .
 \end{aligned} \tag{26}$$

In view of the above two equations (25) and (26) one may treat the $\varphi_{l' m'}$ -term in the Schrodinger equation as a perturbation to the main part

$$\begin{aligned}
 \Delta_r \varphi_{00} &= -4\pi Z \delta(\mathbf{r}) + \sum \sum_{lm} |\psi_{lm}|^2 , \\
 -\frac{1}{2} (\Delta_r - l(l+1)/r^2) \psi_{lm} - \varphi_{00} \psi_{lm} &= E \psi_{lm} ,
 \end{aligned} \tag{27}$$

of these two equations; this perturbation implies a coupling between the orbital momenta (including their magnetic m -components and the spin degeneracy, *i.e.* the spin-orbitals), like in open shells, so that one may expect both an inversion in the main energy levels and orbital competitions (like the *sd*-competition, for instance); an inversion in the main energy levels may also be expected from the main equations written above; in fact, their solutions are degenerate with respect to m , so that we may label them ψ_l , or, introducing the radial quantum number $n = 0, 1, \dots$ (the principal quantum number is now $n + l + 1$), we may also write these equations as

$$\begin{aligned}
 -\frac{1}{2} (\Delta_r - l(l+1)/r^2) \psi_{nl} - \varphi_{00} \psi_{nl} &= E \psi_{nl} , \\
 \Delta_r \varphi_{00} &= -4\pi Z \delta(\mathbf{r}) + 2 \sum_{nl} (2l+1) |\psi_{nl}|^2 ;
 \end{aligned} \tag{28}$$

they may be solved variationally; indeed, $\psi_{nl} \sim r^l$ for $r \rightarrow 0$, while for $r \rightarrow \infty$ one may assume an exponential behaviour of the form $e^{-q_{nl}r/2}$; therefore, we may look for ψ_{nl} as

$$\psi_{nl} = \sum_{i=0} A_{nl}^i r^{l+i} e^{-q_{nl}r/2} , \tag{29}$$

where the polynomial coefficients A_{nl}^i are determined by requiring the orthogonality (not necessarily for radial functions with different values of l) and the normalization; the summations over i depend on how many states we include, for instance, $n = 0, \dots, 5$ for $l = 0$, $n = 0, \dots, 4$ for $l = 1$, and so on, up to, say, $l = 6$ (the calculations must be carried out for each Z , as well as for the ground-state, or for each excited state); this way, we are only left with the parameters q_{nl} , which can be determined variationally by Rietz' procedure, leading thus to a coupled system of equations for q_{nl} ; of course, in order to carry out the variational approach one needs the self-consistent field φ_{00} ; it may be found by assuming

$$\varphi_{00} = \sum_{nl} \frac{\chi_{nl}(r)}{r} e^{-q_{nl}r} , \tag{30}$$

where $\chi_{nl}(r)$ are polynomials, such that $\sum_{nl} \chi_{nl}(0) = Z$; indeed, one can see this from Poisson's equation (28), where $-4\pi Z \delta(\mathbf{r})$ may be replaced by $\Delta_r(Z/r)$, and then, making use of the radial laplacean given by (21), the polynomials χ_{nl} are completely determined (up to the q_{nl} -parameters, of course); the superposition (30) of screened Coulomb and polynomial potentials are reminiscent

of the screened Coulomb potential obtained within the quasi-classical description; one may simplify even further the treatment by assuming only one global q -screening parameter for the potential,

$$\varphi = \frac{Z}{r} e^{-qr} \quad , \quad (31)$$

and determine this q -parameter by minimizing the total energy.

One may expect to get, by following up this approach, the inversions in the periodic table (like $4s3d$, for instance), and, in this context, it is worth noting the effective radial potentials $l(l+1)/2r^2 - \varphi$ in (28), which include the repulsive centrifugal potentials $l(l+1)/2r^2$; these effective potentials for $l \neq 0$ have a sudden fall at small distances and a very long increasing tail for large distances, such that they may accomodate high-energy (bound) states, slightly separated in energy. This suggests a more adequate approach for computing the low-lying excited electron states of a heavy atom; indeed, first one should solve the ion problem, *i.e.* a $+Ze$ charge for the nucleus and $Z-1$ electrons, by a quasi-classical description; [15] one determines this way the chemical potential ($-\varphi_0$, or the ionization potential φ_0 of an atom) and the self-consistent field φ ; then, the high-energy levels of an electron moving in this field can be computed within the quasi-classical description. First, the equation (1) becomes now

$$\hbar^2 k_F^2 / 2m - e\varphi = -e\varphi_0 \quad , \quad (32)$$

and one assumes that the electrons are confined within the region where $\varphi - \varphi_0 > 0$ (the ion having therefore a finite radius); one may use the linearized approach and solve Poisson's equation

$$\Delta\varphi = -4\pi e Z \delta(\mathbf{r}) + q^2(\varphi - \varphi_0) \quad (33)$$

(where φ_0 may be included under the laplacean) within this region, and $\Delta\varphi = 0$ outside, with $\varphi \sim e/r$ at infinite as a boundary condition; once it solved for φ , and determined both φ_0 and the radius of the allowed region, we may pass to look for the electron energy levels in the potential energy $-e(\varphi - \varphi_0)$; [16] the quasi-classical levels are given by the Bohr-Sommerfeld quantization rules

$$\int p_r dr = \int \left[2 \left(E - l(l+1)/2r^2 + \varphi - \varphi_0 \right) \right]^{1/2} dr = 2\pi\hbar(n + \gamma) \quad , \quad (34)$$

where p_r is the classical momentum, the integration is taken along a complete classical orbit, and γ is a quantal correction (or "defect", which may be determined from the boundary conditions of the wavefunctions; here, for a central field $\gamma = 1/2$); [17] the results are suitable for electron states which are high in energy, so that it is more appropriate to use the quasi-classical $(l+1/2)^2$ instead of $l(l+1)$; for highly excited states, where the electron feels practically the Coulomb field e/r , one obtains the Rydberg levels $E_n = -1/2(n + \gamma_l)^2$; one may also note that the small separation ΔE in energy levels, around a certain quasi-classical level E , is given by

$$\Delta E \int \partial p_r / \partial E \cdot dr = \Delta E \int dr / v_r = \Delta E \cdot T = 2\pi\hbar \quad , \quad (35)$$

where v_r is the radial velocity and T is the corresponding classical period of motion; and this is the content of the correspondence principle; the number of energy levels may also be estimated within the quasi-classical approximation, as follows: for a potential energy U , such that $E = p^2/2m + U < 0$, the maximum value of the momentum p is $p_{\max} = (-2mU)^{1/2}$, and the number of levels is given by

$$\frac{1}{(2\pi\hbar)^3} \frac{4\pi}{3} \int d\mathbf{r} \cdot p_{\max}^3 = \frac{1}{(2\pi\hbar)^3} \frac{4\pi}{3} \int d\mathbf{r} \cdot (-2mU)^{3/2} \quad , \quad (36)$$

the integration being carried out over the region where $U < 0$; for a central field the orbital degeneracy reduces the above formula to

$$\frac{1}{2\pi\hbar} \int dp_r dr = \frac{1}{2\pi\hbar} \int dr \left[-2m(U + \mathbf{l}^2/2mr^2) \right]^{1/2} , \quad (37)$$

so that the number of levels is obtained by integrating over dl/\hbar ; one gets

$$\frac{m}{4\hbar^2} \int dr (-U)r . \quad (38)$$

It is also known how to estimate which new l -orbitals appear for what Z ; indeed, one must have

$$-\frac{Ze^2}{r} e^{-qr} + \frac{\hbar^2}{2mr^2} (l + 1/2)^2 = 0 , \quad (39)$$

$$\frac{Ze^2}{r^2} e^{-qr} + \frac{Ze^2}{r} qe^{-qr} - \frac{\hbar^2}{mr^3} (l + 1/2)^2 = 0 ,$$

whence, by using $q = 0.77Z^{1/3}a_H^{-1}$, one obtains $Z = 0.13(2l + 1)^3$; for $0.17(2l + 1)^3$ one gets $l = 1, 2, 3, ..$ for $Z = 5, 21, 58, ..$, in agreement with the periodic table of elements. Turning back to the single-electron levels around the chemical potential φ_0 , they determine this way the lowest excited states of the atom, and provide also an estimation of the small, irregular, quasi-periodic variations of the ionization potentials. One may treat in a similar manner the electron affinity of the atoms, *i.e.* the problem of the negative ion,[18] where, however, a potential barrier occurs for the additional electron.

The energy levels of the atoms and the corresponding wavefunctions are relevant for computing the intensities of the atomic spectra; as well as for the atom response to various external fields, like the electric or magnetic fields, where the Stark effect, the electric polarizability, the diamagnetic susceptibility, the magnetic momentum, the (normal and anomalous) Zeeman effects are of interest.

The extension of Hartree's equations (18) and (19) to molecules and solids are called the density functional equations;[19] usually, these equations includes an exchange contribution, provided by the local variation of the total exchange energy, which depends on density; since the latter involves spin correlations, the equations are also called spin density, or local spin density equations; they are developments of previous theories, like the self-consistent molecular orbitals,[20] or the "cellular" method of metals.[21]

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