Journal of Theoretical Physics

Excited states of heavy atoms

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Abstract

The problem of the energy spectrum of the heavy atoms is briefly reviewed, with emphasis on the single- *vs* many-particle picture, self-consistent Hartree-Fock equations and mean-field concept. Also, the stability, binding energy and collective excitations of heavy atoms within the framework of the linearized Thomas-Fermi model are briefly reviewed. Single-particle excitations are derived for heavy atoms within the linearized Thomas-Fermi model.

Introduction. We consider a heavy atom with nuclear charge Ze, $Z \gg 1$, and Z electrons with mass m and charge $-e$ each; the nucleus is assumed to be fixed. The electrons and the nucleus interact by Coulomb forces and the motion of the electrons is non-relativistic; we neglect the relativistic corrections. The assembly of electrons is described by a wavefunction $\psi(t, \mathbf{r}_1, ... \mathbf{r}_Z)$, where t denotes the time and $\mathbf{r}_i$, $i = 1, 2, ...Z$, is the position of the i-th electron. This wavefunction must be properly symmetrized according to the spin of the atom, which in non-relativsitic approximation is conserved. The wavefunction ψ is the solution of the Schrodinger equation

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi \ ,$$

$$H = -\frac{\hbar^2}{2m}\Delta_i - Ze^2 \sum_i \frac{1}{r_i} + \frac{e^2}{2}\sum_{i \neq j}\frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \ ,$$

(1)

where $\hbar$ is Planck's cosntant; we can see in the hamiltonian H the electron-nucleus Coulomb attraction and the electron-electron Coulomb repulsion. The energies E are given by $H\phi = E\phi$, where $\psi = e^{-\frac{i}{\hbar}Et}\phi$. The Coulomb potential

$$\varphi(\mathbf{r}) = \frac{Ze}{r} - e\sum_i' \frac{1}{|\mathbf{r} - \mathbf{r}_i|}$$

(2)

acting on an electron placed at $\mathbf{r}$ satisfies the Poisson equation

$$\Delta\varphi = -4\pi Ze\delta(\mathbf{r}) + 4\pi e\sum_i' \delta(\mathbf{r} - \mathbf{r}_i) \ ,$$

(3)

where we can recognize the charge density of the central nucleus and of the electrons placed at $\mathbf{r}_i$; the prime over the summation sign means the exclusion of the electron acted by the potential.

It is hopeless to have a solution of the problem formulated above. We are only left with classifying the atomic energies in terms of the total orbital momentum and total spin, which are

both conserved within the non-relativistic approximation (together with the parity); the various spatial orientation of these operators implies a degeneration of these atomic states; we expect a fine-structure splitting arising from relativistic spin-orbit and spin-spin corrections.

An important simplification arises when we assume that the wavefunction is constructed from symmetrized products of single-particle states; the Hartree-Fock system of self-consistent coupled equations is then obtained, whose (numerical) solution is attainable for light atoms, in pretty good agreement with the atomic spectroscopy. However, it is conceivable that the ground state of the complex atoms remains a multi-particle state, and the excited states of these atoms are quasi-particle or collective excitations, with a finite lifetime, irreducible, rigorously, to single-particle constructions.

We note that an electron density can be defined by

$$n(t, \mathbf{r}) = \int' d\mathbf{r}_1 ... d\mathbf{r}_Z \left| (\psi(t, \mathbf{r}_1, ... \mathbf{r}_Z)) \right|^2 \quad , \tag{4}$$

where the prime means integration over all positions except $\mathbf{r}$, which appears in the mean potential energy in equation (1); the variation of $(\psi, H\psi)$ leads to Schrodinger equation (1); the use of a Hartree-Fock approximation to ψ has the inconvenient that the density depends on the set of single-particle states included in the Hartree-Fock approximation (the variation of $(\psi, H\psi)$ in this case leads to the Hartree-Fock equations); this inconvenient can be removed by using a field operator ψ, which includes all the single-particle states; however, there still remains the basic drawback of using single-particle states. We note also that there is no equilibrium density $n(\mathbf{r})$ for the potential (interaction) energy in the ground state, except the collapse $\mathbf{r}_i = 0$, as expected. Stable states may only exists for moving electrons, as in the classical mechanics, and then their radiation should vanish; a point ensured by the quantum-mechanics.

The existence of the Coulomb potential φ suggests a very useful approximation, known as the mean-field approximation (due to Bohr): we may assume that each electron moves in a field generated by the nucleus and the rest of the electrons. In the first approximation, at least for the ground state, we may assume that the mean field is a centrally-symmetric field; then, the electron states are caracterized by an orbital number l (with the corresponding orbital degeneracy), a principal number n and the spin orientation; we may construct the ground state of the atom and the excited states by such electronic configurations, in much the same manner as for a hydrogen atom; we may have closed shells, where the total orbital moment and the total spin are zero, and open shells whose filling are given by Hund's semi-empirical rules (first get the highest spin in the open shell, then the highest possible orbital momentum; rules derived from minimizng the Coulomb repulsion between the electrons and the highest possible symmetry); connection with the states classified according to the total orbital momentum and the total spin can be made. When confronted with the Mendeleev periodic table and the irregular variation with Z of the ionization potentials, we find that there should be inversions in filling up the hydrogen-like mean-field shells: for instance, the shell $4s$ appears before the shell $3d$, $5s$ appears before $4d$, $6s$ before $5d$, $5d$ before $4f$, etc (with notation nl). After finding the electronic states of the mean-field potential, we construct the electron density for a given configuration and check the Poisson equation of the mean-field for consistency; corrections are then necessary, such that the mean-field is different for each electron state and depends on the configuration; there is no definite rule to attain consistency, which means that the self-consistent solution is impossible, in fact. This indefiniteness is specific to our working with single-particle states.

Linearized Thomas-Fermi model.[1, 2] Working with the single-particle picture seems un-avoidable (and we should be content with the ensuing errors), but we can minimize the effect

of this picture; this can be achieved by using the Fermi statistics and, for heavy atoms, the quasi-classical approximation, in the linearized Thomas-Fermi model. We note that heavy atoms are strongly bound, such that the highest-state electrons have a high spatial variation of their wavefunctions; that means that the nucleus is screened by the lowest-state electrons and we may use the quasi-classical approximation for the highest-state electrons. Therefore, we may assume that the electrons ocupy quasi-free states uo to a Fermi level which depends on the position. Then we have a dependence of the density $n \sim \varphi^{3/2}$ on the potential φ, through $n \sim k_F^3$ and $\varphi \sim \varepsilon_F \sim k_F^2$, where k_F is the Fermi wavevector and ε_F is the Fermi level. We note that the Fermi sea is inert in the dynamics, and only the Fermi surface does act. This is the well-known standard "3/2" Thomas-Fermi model, which exhibits some well-known inconveniences. These drawbacks originate in not keeping the quasi-classical approximation consistently: at those positions where k_F varies strongly (*i.e.* near the nucleus and far away from the nucleus), these variations are amplified by powers like k_F^2 and k_F^3; consequently, we adop a linearized form by replacing these powers by $q^2 k_F$ and, respectively, $q^4 k_F$, such that $n \sim q^2\varphi$, q being a variational parameter which is determined from the minimum of the energy. Thus, the Poisson equation has the screened solution $\varphi = (Ze)e^{-qr}/r$ and we get a consistent picture of the ground state. The linearization and the variational character of the parameter q account for multi-particle character of the picture; the functional dependences on q derived from the quasi-free particle Fermi model still reflect the starting single-particle character. The strong spatial variations of the potential near the nucleus and the corresponding deviations from the quasi-classical approximation may be accounted for by a Hartree-type perturbation-theory correction, while the exchange energy brings only a minor contribution of at most 4% to the total energy; the overall error of the linearized Thomas-Fermi model is of the order 5%. The binding energy $-15.84 Z^{7/3} eV$ is obtained within the linearized Thomas-Fermi model, which is in good agreement with the empirical estimation $-16 Z^{7/3} eV$.

The overall picture obtained for the ground state of a heavy atom within the linearized Thomas-Fermi model is an electron density $n = (Zq^2/4\pi)e^{-qr}$, the electrons being acted by the screened potential $\varphi = (Ze)e^{-qr}/r$ (with a Hartree-type correction to the total energy). The ground-state energy is obtained from the minimum of an energy function $\mathcal{E}(q)$, which leads to $q \simeq Z^{1/3}/a_H$, where $a_H = \hbar^2/me^2 \simeq 0.53$Å is the Bohr radius. The radial electron density $4\pi r^2 n(r) = (Zq^2)r^2 e^{-qr}$ has a maximum for $r = R$, $qR \simeq 1$, such that we may take $R \simeq a_H/Z^{1/3}$ as the radius of the atom. We can see that heavy atoms are more tightly bound than light atoms, as a consequence of the factor $Z^{-1/3}$ in their radius R; this radius lies in between the radius of the first Bohr orbit a_H/Z and the Bohr radius a_H (which may be viewed as the maximum extent of the atom).

Collective excitations. The collective excitations of heavy atoms in the linearized Thomas-Fermi model are given by the energy variation about its equilibrium value, due to the variation of the parameter q. Since the equilibrium is attained for $qR \simeq 1$, it follows that these excitations correspond to variations $\delta R = u \simeq -\delta q/q^2$, *i.e.* to radial vibrations. From the energy function $\mathcal{E}(q)$ expanded in power series of $\delta q = -q^2 u$ we get the frequency ω_0 of these (harmonic) vibrations as

$$\hbar\omega_0 \simeq \frac{Ze^2}{a_H} = Z\frac{\hbar^2}{ma_H^2} \simeq 28 Z eV \; ; \tag{5}$$

this energy is in the range of moderate X-rays, as expected. Of course, these collective excitations are quantum-mechanical oscillators with coordinate u; they are normal modes of vibrations of the atom.

If the atom is subject to an electric field directed along an axis, the equilibrium condition gives $\delta q = -q\delta R/R = -q^2\delta R$, where $\delta R = u\cos\theta$, where u is the displacement of the electrons and θ is the angle made by **R** with the direction of the electric field. The variation $\delta q = -q^2 u\cos\theta$ depends

now on the angle θ, such that we should use for the variation of the energy $(1/2)\int d\theta \sin\theta \delta\mathcal{E}(q)$; this gives a factor $1/\sqrt{3}$ in front of the frequency given above. It follows the polarization energy $\delta\mathcal{E} \simeq (a_H^3/Z)E^2$ for a static electric field E, and the polarizability $\alpha \simeq a_H^3/Z$. The vibrations induced by an external electric field, varying periodically in time, are called giant atomic-dipole oscillations; they exhibit a resonance for $\omega = \omega_0$, where ω is the frequency of the field.[2]

The change in energy implies also anharmonicities, which, for weak external forces (*e.g.*, electric fields) generate higher-order harmonics radiation; for a sudden application of weak external forces the electrons are re-configured and a stationary regime of higher-order harmonics radiation is attained. If the external field is higher, ionization may appear (as estimated in Ref. [2]).

Single-particle excitations. Within the linearized Thomas-Fermi model the electrons move in the potential $\varphi(r) = (Ze/r)e^{-qr}$, where $q \simeq Z^{1/3}/a_H$; this is a self-consistent mean-field pseudo-potential, in the sense that it may be suitable for global properties, but not for single-particle properties. There is no analytical solution of the Schrodinger equation with this potential. We can approximate it by an effective Coulomb potential $\overline{\varphi}(r) = (Ze/r)\overline{e^{-qr}}$, where the average is taken over the spherical volume with radius $R = 1/q$; we get $\overline{\varphi}(r) = Z^*e/r$, where the effective (screned) nuclear charge is $Z^* = Z\overline{e^{-qr}} \simeq 0.5Z$ electron charges. The effective Coulomb potential $\overline{\varphi}(r) = Z^*e/r$ may be used to get approximate single-particle excitations. Indeed, the hydrogen-like energy levels in this potential are $\mathcal{E}_n = Z^{*2}e^2/2a_Hn^2$, where $n = 1, 2, ...$. These energy levels are filled up to some maximum value N, which, in the Thomas-Fermi model of quasi-free electrons is given by $N^3 \simeq Z$ and in the hydrogen-like model is given by $\sum_{n=1}^{N} 2\sum_0^{n-1}(2l+1) \simeq N^3 \simeq Z$; we note that the orbital number l takes valus $0, 1, ...n-1$ and orbital and spin degeneracies are removed in the quasi-free electron model. Therefore, we may assume $N \simeq Z^{1/3}$ and the maximum value of the orbital number for the highest level $L = N - 1$.[1] It follows that the single-particle excitatiosn are given by

$$\delta E_N(\delta n) = \delta(Z^{*2}e^2/2a_HN^2) = (Z^{*2}e^2/a_HN^3)\delta n \simeq$$

$$\simeq \frac{Z^{*2}e^2}{Za_H}\delta n \quad , \tag{6}$$

where $\delta n = 1, 2, 3...$; these energy levels are separated by $\simeq 7ZeV$; these energy levels are lower than the energy of the collective excitations. It is well known that perheral elctrons with a $Z - 1$, $Z - 2$, ... core have much lower energy levels.

There may exist another method of estimation of the single-particle excitations starting with the Schrodinger equation

$$-\frac{\hbar^2}{2m}\Delta\psi - \frac{Z^*e^2}{r}\psi = \mathcal{E}\psi \tag{7}$$

with $\psi = RY_{lm}$, where Y_{im} are the spherical functions; the radial equation is

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \left[-\varepsilon - \left(\frac{L^2}{r^2} - \frac{2Z^*}{a_Hr}\right)\right]R = 0 \quad , \tag{8}$$

where $\varepsilon = 2m \mid \mathcal{E} \mid /\hbar^2$ ($\mathcal{E} < 0$) and $L^2 = l(l+1)$; the effective potential

$$V = \frac{L^2}{r^2} - \frac{2Z^*}{a_Hr} \tag{9}$$

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[1]It is worth noting that the formula $Z \simeq N^3 = (L+1)^3$ gives the atomic number Z when the shell L first appears in the atom; for $L = 1, 2, 3, 4$ we get $Z = 8, 27, 64, 125$ instead of the correct valeus $Z = 5, 21, 58$ and probably $Z = 124$ (p, d, f and g shells).

has a minimum value $-V_0 = -Z^{*2}/L^2 a_H$ for $r_0 = L^2 a_H/Z^*$ and we may expand it in powers of $\rho = r - r_0$ about this point; the equation becomes

$$\frac{1}{\rho^2}\frac{d}{d\rho}\left(\rho^2\frac{dR}{d\rho}\right) - \left(\varepsilon - V_0 + V_2\rho^2 + ...\right)R = 0 \quad, \tag{10}$$

where $V_2 = (1/2)V''(r_0) = Z^{*4}/L^6 a_H^4$. It is convenient to make the substitutions $\rho = \alpha\xi$, $\alpha^2\sqrt{V_2} = 1$ and $R = e^{-\xi^2/2}F$, where

$$F'' + 2\left(\frac{1}{\xi} - \xi\right)F' + (\beta - 3)F = 0 \quad, \quad \beta = \frac{V_0 - \varepsilon}{\sqrt{V_2}} \quad; \tag{11}$$

this equation is solven by a series $F = \sum_{s=0} C_s\xi^{2s}$ with the coefficients C_s satisfying the relation

$$\frac{C_{s+1}}{C_s} = \frac{4s + 3 - \beta}{2(s+1)(2s+3)} \quad; \tag{12}$$

the series terminates at some integer $s = 0, 1, 2, ...$ given by $\beta = 4s + 3$, whence we get the energy levels

$$\mathcal{E}_s = -\frac{Z^{*2}e^2}{2a_H L^2} + \frac{Z^{*2}e^2}{2a_H L^2}\frac{4s+3}{L} \quad. \tag{13}$$

This formula is valid for rather unrealistic case $L = N - 1 \gg 1$, where it may be written as

$$\mathcal{E}_s = -\frac{Z^{*2}e^2}{2a_H\left(L + \frac{4s+3}{4}\right)^2} = -\frac{Z^{*2}e^2}{2a_H\left(N + s - 1/4\right)^2} \quad, \tag{14}$$

which exhibits a Rydberg correction $(s - 1/4)$ to hydrogen-like energy levels. Equation (13) imposes a rather severe constraint $s < (L - 3)/4 = N/4 - 1$ for realistic cases, which originates in the series expansion of the effective potential V (this series seems to converge slowly). Leaving aside this constraint, equation (13) gives excited energy levels

$$\delta E_s = \frac{Z^{*2}e^2}{a_H L^3}\cdot 2s \quad, \tag{15}$$

which agrees qualitatively with equation (6) (for $L = N - 1 \gg 1$).

References

[1] L. C. Cune and M. Apostol, "On the atomic binding energy in the Thomas-Fermi model", Roum. J. Phys. **55** 913-919 (2010).

[2] M. Apostol, "Giant dipole oscillations and ionization of heavy atoms by intense electromagnetic fields", Roum. Reps. Phys. **67** 837-853 (2015).