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Dynamics of the electron cloud of heavy atoms in an external electric field

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

Abstract

The dynamics of the electron cloud of heavy atoms in an external, oscillating electric field is analyzed within the linearized Thomas-Fermi theory. It is shown that the electron screening reduces appreciably the magnitude of the external fields with optical frequencies, while the electron motion generates an additional, internal electric field, oscillating with the much higher frequency of the atomic dipolar eigenmodes. A resonant regime is identified for external frequencies close to the hiher eigenfrequencies, which may lead to an appreciable increase of the internal electric field in heavy atoms.

Global dynamics. We adopt here the linearized Thomas-Fermi theory for heavy atoms, *i.e.* for atoms with atomic number $Z \gg 1$. This theory gives the correct binding energy of heavy atoms ($-16Z^{7/3}eV$) and predicts giant dipole oscillations of the electron cloud.[1] We describe in this paper the dynamics of the electron cloud of such atoms in an external, oscillating electric field $E = E_0 \sin \omega t$, with amplitude E_0 and frequency ω, oriented along the z-axis.

According to this theory, the electrons in heavy atoms move in a self-consistent screened potential $\varphi = (Ze)e^{-qr}/r$ and the equilibrium electron distribution is $n = (Zq^2/4\pi)e^{-qr}/r$, where $-e$ is the electron charge, r is the distance from the atomic nucleus and q is a variational parameter (Thomas-Fermi screening wavevector) which is determined from the minimum of the energy. The total energy of the electrons is a function $W(q)$; it may be expanded in powers of $\delta q = q - q_0$ about the equilibrium value q_0 of the screening wavevector as

$$W = W_0 + W_1\delta q + \frac{1}{2}W_2\delta q^2 + ... \ , \tag{1}$$

where $W_0 = W(q_0)$, $W_1 = \partial W/\partial q \mid_{q_0}$, $W_2 = \partial^2 W/\partial q^2 \mid_{q_0}$. At equilibrium $W_1(q_0) = 0$; this equation which gives the equilibrium value of the screening wavevector $q_0 = (6/\pi^2)^{1/3}Z^{1/3}/a_H$, where $a_H = \hbar^2/me^2 \simeq 0.53$Å is the Bohr radius ($\hbar$ is Planck's constant and m is the mass of the electron).[1] We can see that the radial distribution $r^2 n$ of the electrons has a maximum for $R_0 = 1/q_0 \sim a_H/Z^{1/3}$; equation (1) can be re-written as

$$W = W_0 + \frac{1}{2}W_2\delta R^2 + ... \ , \tag{2}$$

with new functions $W_{0,2}$ of R_0; for instance, $W_2 = \partial^2 W/\partial R^2 \mid_{R_0}$, where $R = 1/q$. We introduce the notation $W_2 = Zm\omega_0^2$ in equation (2), where[1]

$$\omega_0^2 = \frac{27}{2\pi^2}\frac{Z^2e^2}{ma_H^3} \ ; \tag{3}$$

we recognize in equation (3) a plasma frequency with an average electron density of the order $Z/(a_H^3/Z)$; indeed, the effective volume is of the order a_H^3/Z (linear dimension $a_H/Z^{1/3} \sim 1/q_0$). The frequency ω_0 corresponds to the energy $\hbar\omega_0 \simeq 28 \cdot Z(eV)$ ($\omega_0 \simeq 4.5Z \times 10^{16} s^{-1}$). It is easy to see from equation (2) that ω_0 is the eigenfrequency of atomic dipolar breathing mode with the dynamical coordinate δR; equations (2) predict a giant atomic dipolar resonance for $\omega = \omega_0$; damping shold be included, which is given by radiation loss; at resonance, higher-order terms should also be included, arising in the expansion of the energy W (equation (2)); they lead to the ionization of heavy atoms, as described by the linearized Thomas-Fermi theory.[1]

The electric field produces a global, uniform displacement u of the electron cloud, along the z-direction; this displacement changes the density and, therefore, it changes also the parameter R_0; the change is $\delta R = u\cos\theta$, where θ is the angle made by the radius R with the direction of the external field (the z-direction). We can see that this change is local (it depends on θ); in these conditions we should re-write the energy W as

$$W = W_0 + \frac{1}{2}\int d\mathbf{r} w_2 u^2 \cos^2\theta + ... \quad , \tag{4}$$

where the density w_2 does not depend on position; it is W_2/V, V being the volume of integration. From equation (4) we get

$$W = W_0 + \frac{1}{2} Z m \omega_0^2 u^2 + ... \quad , \tag{5}$$

where ω_0 is now given by

$$\omega_0^2 = \frac{9}{2\pi^2}\frac{Z^2 e^2}{m a_H^3} \ ; \tag{6}$$

a factor $1/3$ occurs in the new squared frequency, which amounts to averaging $\cos^2\theta$. We write this squared frequency as $\omega_0^2 = 4\pi\overline{n}e^2/m$, where the average density is $\overline{n} = (9/8\pi^3)Z^2/a_H^3$.

The equation of motion of the coordinate u is

$$\ddot{u} + \omega_0^2 u = -\tfrac{eE_0}{m}\sin\omega t \quad , \tag{7}$$

with the solution (with vanishing initial conditions)

$$u = \tfrac{eE_0}{m(\omega^2-\omega_0^2)}\left(\sin\omega t - \tfrac{\omega}{\omega_0}\sin\omega_0 t\right) \quad , \tag{8}$$

The above description assumes a displacement much smaller than the dimension of the atom. The displacement given by equation (8) satisfies this condition for any reasonably high electric field, since ω_0 is a high frequency ($\omega \ll \omega_0$); indeed, from equation (8) we get $E_0 \ll (m\omega_0^2 a_H/e) \simeq 10^7 Z^2 esu$ (the non-relativistic limit for electrons is $E_0 \simeq 10^8 esu$ for $\omega = 10^{15} s^{-1}$, which corresponds to a laser intensity $\simeq 10^{18} w/cm^2$).

Let us assume an assembly of electrical charges q at equilibrium, subject to a local displacement $\mathbf{u}$; such a displacement produces a density change $\delta n = -n div\mathbf{u}$, where n is the equilibrium density; it follows that we have a charge density imbalance $\delta\rho = -nqdiv\mathbf{u}$ and a current density $\delta\mathbf{j} = nq\dot{\mathbf{u}}$; Gauss's equation reads $div\mathbf{E} = -4\pi nqdiv\mathbf{u}$, where $\mathbf{E}$ is the electric field generated by this charge imbalance; or $div(\mathbf{E} + 4\pi nq\mathbf{u}) = 0$. Therefore, the polarization of the assembly is $\mathbf{P} = nq\mathbf{u}$. If the time variations of $\mathbf{u}$ are slow, *i.e.* if the frequency ω of the displacemnt $\mathbf{u}$ is such that $\omega \ll c/l$, where l is the dimension of the assembly, then Gauss's equation has the solution $\mathbf{E}_i = -4\pi\mathbf{P} = -4\pi nq\mathbf{u}$; $\mathbf{E}_i$ is the internal (depolarizing) field. We note that this field appears even if the displacement is uniform, due to the variation of the displacement at the surface of the

assembly (if any); it is a dipolar field. For atoms, it is due to the displacement of the electron cloud with respect to the atomic nucleus.[2]

We apply the above considerations to the results obtained here, with $q = -e$ and $n = \overline{n}$; making use of equation (8), we get the polarization

$$P = -\frac{\overline{n}e^2E_0}{m(\omega^2-\omega_0^2)}\left(\sin\omega t - \frac{\omega}{\omega_0}\sin\omega_o t\right) \tag{9}$$

and the internal electric field

$$E_i = \frac{\omega_0^2E_0}{\omega^2-\omega_0^2}\left(\sin\omega t - \frac{\omega}{\omega_0}\sin\omega_o t\right) \tag{10}$$

(both directed along the external field); also, from equation (9) we can get the polarizability. The total electric field inside the atom is

$$E_t = E_i + E = \frac{\omega^2}{\omega^2-\omega_0^2}E_0\sin\omega t - \frac{\omega\omega_0}{\omega^2-\omega_0^2}E_0\sin\omega_0 t \ ; \tag{11}$$

since $\omega \ll \omega_0$, it can be written as

$$E_t \simeq -\frac{\omega^2}{\omega_0^2}E_0\sin\omega t + \frac{\omega}{\omega_0}E_0\sin\omega_0 t \ . \tag{12}$$

We can see that the external field $E_0\sin\omega t$ is appreciably reduced inside the atom, by a factor $(\omega/\omega_0)^2 \simeq 1.6\times10^{-3}/Z^2$ (for $\omega = 10^{15}s^{-1}$), due to the electron screening; at the same time, there appears inside the atom an electric field with frequency equal to the high atomic eigenfrequency $\omega_0 \simeq 2.6Z\times10^{16}s^{-1}$ (equation (8)), reduced only by the factor $\omega/\omega_0 \simeq 4\times10^{-2}/Z$ in comparison with the amplitude of the external field; we note that both fields act inside the atom (*i.e.*, it acts on the electrons too), the higher-frequency component being able to excite nuclear states. Also, we note that the latter field occurs in any kind of external excitation.

Finally, we note that the self-consistent potential $\varphi = (Ze)e^{-qr}/r$ of the linearized Thomas-Fermi theory consists of the nucleus potential Ze/r and the electron potential $\varphi_e = Ze(e^{-qr}-1)/r$; the latter produces a radial electric field $E_e = -Ze\left[1-(1+qr)e^{-qr}\right]/r^2$, which for $qr \ll 1$ is $E_e \simeq -Zeq^2/2$. The variation of this field with respect to the parameter q gives an internal field $E_i = (Ze/R_0)^3\delta R$, which is of the same order of magnitude as the internal field given by equation (10).

The apreciable reduction in magnitude of the external field obtained here originates in using the same average density $\overline{n}$ both in the frequency given by $\omega_0^2 = 4\pi\overline{n}q^2/m$ and in the internal field $E_i = -4\pi\overline{n}qu$ (where q denotes the charge). This circumstance follows from the general equation of motion. Indeed, Newton's equation of motion along a direction is $m\ddot{u} = qE + qE_i$, where E is the external field and E_i is the internal field; if we write $qE_i = -m\omega_0^2u$, we get the equation of motion $m\ddot{u} + m\omega_0^2u = qE$; the condition $qE_i = -m\omega_0^2u$ is ensured by the two assumptions made here, involving the average density $\overline{n}$.

Local dynamics. The kinetic energy of a free electron gas is $V(\hbar^2k_F^5/10\pi^2m)$, where V is the volume, k_F is the Fermi wavevector and m is the mass of the electron; if k_F varies in space and if the gas is sufficiently dense, we may view a local free electron gas with the kinetic energy $\Delta V(\hbar^2k_F^5/10\pi^2m)$; then, the total kinetic energy may be written as

$$E_{kin} = \int d\mathbf{r}\frac{\hbar^2k_F^5}{10\pi^2m} \ , \tag{13}$$

or, using the density $n = k_F^3/3\pi^2$,

$$E_{kin} = \int d\mathbf{r} \frac{3(3\pi^2)^{2/3}}{10} \frac{\hbar^2}{m} n^{5/3} \ ; \tag{14}$$

the total energy of a heavy atom with atomic number Z ($Z \gg 1$) can be written as

$$E = \int d\mathbf{r} \varepsilon_{kin}(n) - Ze^2 \int d\mathbf{r} \frac{n(\mathbf{r})}{r} + \frac{1}{2} e^2 \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \ , \tag{15}$$

where $\varepsilon_{kin}(n) = [3(3\pi^2)^{2/3}/10]\hbar^2 n^{5/3}/m$ is the local kinetic energy; the second term on the right in equation (15) is the Coulomb electron-nucleus attraction and the third term is the Coulomb electron-electron repulsion ($-e$ is the charge of the electron).

The first-order variation of this energy is

$$\delta E^{(1)} = \int d\mathbf{r} \frac{\partial \varepsilon_{kin}}{\partial n} \delta n - Ze^2 \int d\mathbf{r} \frac{\delta n}{r} + e^2 \int d\mathbf{r} d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \delta n \ ; \tag{16}$$

at equilibriun it should be zero, *i.e.*

$$\frac{\partial \varepsilon_{kin}}{\partial n} - \frac{Ze^2}{r} + e^2 \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} = 0 \ ; \tag{17}$$

this equation gives the equilibrium density $n_0(\mathbf{r})$. A convenient way of solving equation (17) is to introduce the self-consistent potential

$$\varphi(\mathbf{r}) = \frac{Ze}{r} - e \int d\mathbf{r}' \frac{n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} \tag{18}$$

and to notice that it satisfies the Poisson equation

$$\Delta \varphi = -4\pi Ze\delta(\mathbf{r}) + 4\pi e n(\mathbf{r}) \ ; \tag{19}$$

equation (17) becomes

$$\frac{\partial \varepsilon_{kin}}{\partial n} - e\varphi = 0 \ , \tag{20}$$

i.e.

$$(3\pi^2)^{2/3} \frac{\hbar^2}{2m} n^{2/3} - e\varphi = 0 \ , \tag{21}$$

or

$$\frac{\hbar^2 k_F^2}{2m} - e\varphi = 0 \ ; \tag{22}$$

this is the Thomas-Fermi model; it is a quasi-classical model; it does not provide the binding of the electrons in atoms.

The basic assumption of the Thomas-Fermi model is a slightly inhomogeneous electron gas; in accordance with this assumption we write $k_F^2 = 2\overline{k}_F k_F$ and $k_F^3 = 3\overline{k}_F^2 k_F$, where $\overline{k}_F$ is a parameter; also, we introduce the parameter $q^2 = 4\overline{k}_F/\pi a_H$, where $a_H = \hbar^2/me^2$ is the Bohr radius; we get $n = (q^2/4\pi e)\varphi$ and a linearized Poisson equation

$$\Delta \varphi = -4\pi Ze\delta(\mathbf{r}) + q^2 \varphi \tag{23}$$

(equation (19)) with the solution $\varphi = (Ze/r)e^{-qr}$ and $n_0 = (Zq^2/4\pi r)e^{-qr}$. Making use of this solution in the total energy given by equation (15) and linearizing its expresion with respect to k_F,

we get the binding energy of the atom as a function of the parameter q; minimizing this energy with respect to q, we get the equilibrium value

$$q = (6/\pi^2)^{1/3}\frac{Z^{1/3}}{a_H} \tag{24}$$

of this parameter; including quantum-mechanical corrections, we get the binding energy $-16Z^{7/3}eV$, in agreement with the experimental data.[1] We can see that the electron density in heavy atoms is concentrated in the region $r < R$, where R is given by $qR = 1$, *i.e.* $R = (\pi^2/6)^{1/3}a_H/Z^{1/3}$, which is a much smaller radius of the atom than the Bohr radius a_H ($Z \gg 1$). The variation of the parameter q (*i.e.* of the "radius" R) leads to the breathing eigenmodes of the atom with the frequency ω_0 given by equation (3); in the presence of an electric field this frequency gives the polarization and the screening of the external electric field, as described above; higher-order terms in the expansion of the energy with respect to the parameter q gives non-linearities which may lead to ionization.[1] All these are related to the global dynamics of the electron cloud of the heavy atoms, which moves as a whole. In order to distinguish the Thomas-Fermi model from the linearized Thomas-Fermi theory we refer sometimes to the former as the 3/2-Thomas-Fermi model (since $n \sim \varphi^{3/2}$ in this model).

Let us investigate the local dynamics of the electron cloud in heavy atoms. First, we note that external electromagnetic fields with wavelengths smaller than the radius R involve not only electric fields, but magnetic fields too; second, for small wavelengths the electromagnetic fields behave as a collection of photons (*e.g.*, X-rays or gamma rays), and their interaction with the electrons is quantum-mechanical; third, the linearized Thomas-Fermi theory is not valid for distances too close to the atomic nucleus (where quantum-mechanical corrections should be included). Therefore, we may leave aside such small spatial variations of the electron density. On the other hand, we notice that the number of electrons inside the sphere with radius R is $Z(1-2/e) \simeq 0.27Z$, while the number of electrons outside this sphere is $2Z/e \simeq 0.73Z$; we can see that it is meaningful to consider electromagnetic fields with small spatial variations (long wavelengths), which affect mainly the tail of the electron density in heavy atoms; in this case, we may neglect the magnetic field (this treatment may be termed a quasi-dipolar approximation).

The second-order variation of the total energy E given by equaton (15) is

$$\delta E^{(2)} = \frac{1}{2}\int d\mathbf{r}\frac{\partial^2\varepsilon_{kin}}{\partial n^2}(\delta n)^2 + \frac{1}{2}e^2\int d\mathbf{r}d\mathbf{r}'\frac{\delta n(\mathbf{r})\delta n(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \quad , \tag{25}$$

where the derivatives are taken for $n = n_0$. We represent the density variations as $\delta n = -n_0 div\mathbf{u}$, where $\mathbf{u}(t,\mathbf{r})$ is a displacement field; these variations ensure the conservation of the total number of electrons; the second-order variation of the total energy becomes

$$\delta E^{(2)} = \frac{1}{2}\int d\mathbf{r}\frac{\partial^2\varepsilon_{kin}}{\partial n^2}n_0^2(div\mathbf{u})^2 + \frac{1}{2}e^2\int d\mathbf{r}d\mathbf{r}'n_0(r)n_0(r')\frac{div[\mathbf{u}(\mathbf{r})]\cdot div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|} \ ; \tag{26}$$

with the kinetic energy

$$T = \frac{m}{2}\int d\mathbf{r}n_0\dot{u}^2 \tag{27}$$

of the displacement field $\mathbf{u}$ we get the lagrangian of this field

$$L = \frac{m}{2}\int d\mathbf{r}n_0\dot{u}^2 - \frac{1}{2}\int d\mathbf{r}\frac{\partial^2\varepsilon_{kin}}{\partial n^2}n_0^2(div\mathbf{u})^2 - \frac{1}{2}e^2\int d\mathbf{r}d\mathbf{r}'n_0(r)n_0(r')\frac{div[\mathbf{u}(\mathbf{r})]\cdot div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|} \ ; \tag{28}$$

the equation of motion for the field $\mathbf{u}$ is

$$mn_0\ddot{\mathbf{u}} - grad\left[\left(\frac{\partial^2\varepsilon_{kin}}{\partial n^2}\right)n_0^2 div\mathbf{u}\right] - e^2 grad\left[n_0\int d\mathbf{r}'\frac{n_0(r')div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}\right] = n_0\mathbf{F}_{ex} \quad , \tag{29}$$

where $\mathbf{F}_{ex}$ is the external force; or

$$m\ddot{\mathbf{u}} - \frac{(3\pi^2)^{2/3}\hbar^2}{3mn_0}grad\left(n_0^{5/3}div\mathbf{u}\right) - \frac{e^2}{n_0}grad\left[n_0\int d\mathbf{r}'\frac{n_0(r')div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|}\right] = \mathbf{F}_{ex} \ . \tag{30}$$

In the long-wavelength limit the density is, practically, a constant $n_0 = \overline{k}_F^3/3\pi^2 = 3Z^2/16\pi^3 a_H^3$ (we may see that the Z electrons are included in a volume with dimension of the order $a_H/Z^{1/3} \simeq R$); this density is comparable with the average density $\overline{n}$ in equation (6); equation (30) becomes

$$m\ddot{\mathbf{u}} - \frac{(3\pi^2)^{2/3}\hbar^2}{3m}n_0^{2/3}grad\cdot div\mathbf{u} - e^2 n_0 grad\int d\mathbf{r}'\frac{div[\mathbf{u}(\mathbf{r}')]}{|\mathbf{r}-\mathbf{r}'|} = \mathbf{F}_{ex} \ ' \tag{31}$$

for an external plane wave $\mathbf{F}_{ex} = -e\mathbf{E}_0 e^{-i\omega t + i\mathbf{kr}}$ ($c/\omega \gg a_H/Z^{1/3}$, where c is the speed of light in vacuum) and $\mathbf{E}_0$ is the amplitude of the electric field, the solution is $\mathbf{u} = \mathbf{u}_0 e^{-i\omega t + i\mathbf{kr}}$; the amplitude of the displacement field is given by

$$\omega^2\mathbf{u}_0 - \omega_0^2\frac{(\mathbf{ku}_0)\mathbf{k}}{k^2} - v^2(\mathbf{ku}_0)\mathbf{k} = e\mathbf{E}_0 \quad , \tag{32}$$

where

$$\omega_0^2 = \frac{3}{4\pi^2}\frac{Z^2e^2}{ma_H^3} \tag{33}$$

and

$$v^2 = \frac{3^{1/3}}{(16\pi)^{2/3}}\frac{\hbar^2 Z^{4/3}}{m^2 a_H^2} \ . \tag{34}$$

We can see that the longitudinal displacement is

$$\mathbf{u}_0 = \frac{e\mathbf{E}_0}{\omega^2 - \Omega^2} \tag{35}$$

with the frequency of the eigenmodes given by

$$\Omega^2 = \omega_0^2 + v^2k^2 \ ; \tag{36}$$

these modes are dispersive plasmons; they are the breathing modes derived above (now dispersive). The plasma frequency ω_0 given by equation (33) is comparable with the plasma frequency given by equations (3) and (6); it arises from the Coulomb repulsion (at equilibrium); the Fourier transform of the Coulomb potential is involved in its expression. The velocity v ($v \ll c$) arises from the variation of the kinetic energy. Equation (35) shows that the screening is present, as described above; the full solution of eqution (31) includes the excitation of the eigenmodes too. From equation (32) we can see that the transverse modes are free.

Finally, we note in equation (31) that a global displacement u implies $grad\cdot div\mathbf{u}$ of the order u/a^2, where $a \simeq a_H/Z^{1/3}$; in this case the Coulomb repulsion in equation (31) is vanishing and the kinetic term gives a frequency $\omega \simeq \omega_0$.

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