

GIANT DIPOLE OSCILLATIONS AND IONIZATION OF HEAVY ATOMS BY
INTENSE ELECTROMAGNETIC FIELDS

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Abstract. The "empirical" binding energy $-16Z^{7/3}eV$ of heavy atoms (atomic number $Z \gg 1$) is computed by a linearized version of the Thomas-Fermi model, including a Hartree-type correction. The computations are carried out by means of a variational approach. Exchange energy and corrections to the exchange energy are also estimated. This is an updated result. It is shown that giant dipole oscillations of the electrons may be induced in heavy atoms by external electromagnetic fields in the range of moderate X -rays, which, in intense fields, may lead to ionization. There are examined anharmonicities in the giant dipole oscillations, which lead to frequency shifts and high-order harmonics. Transitions to excited states and ionization of "peripheral" electrons are also investigated in the quasi-classical approximation for heavy atoms.

Key words: heavy atoms, Thomas-Fermi theory, giant dipole resonance, ionization.

1. INTRODUCTION. THOMAS-FERMI MODEL

The Thomas-Fermi model is based on the quasi-classical description and the statistical character of the electron single-particle states in heavy atoms, *i.e.* in atoms with large atomic numbers Z ($Z \gg 1$). [1]-[4] The electrons are assumed to form an inhomogeneous, dense gas of fermions, slightly perturbed by the nuclear charge Ze , where $-e$ is the electron charge. The singular character of the nuclear Coulomb potential Ze/r at the origin is compensated by its relatively small range around the origin, which is left by the electron screening; this particularity justifies the perturbation character of the Coulomb potential.

Usually, the Fermi wavevector k_F is determined by a self-consistent field potential φ , according to

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

where \hbar is Planck's constant and m is the electron mass. Equation (1) expresses the

energy conservation, with zero total energy for neutral atoms. The electric potential φ is determined by Poisson's equation

$$\Delta\varphi = -4\pi Ze\delta(\mathbf{r}) + 4\pi ne, \quad (2)$$

where the electron density is given by $n = k_F^3/3\pi^2 = (1/3\pi^2)(2me/\hbar^2)^{3/2}\varphi^{3/2}$, as for a Fermi gas; equation (2) becomes "the 3/2"-equation, which is solved numerically with the boundary condition $\varphi r \rightarrow 0$ for $r \rightarrow \infty$ (and $\varphi = Ze/r$ for $r \rightarrow 0$).[5] The atomic binding energy, as computed by means of this theory,[4, 6, 7] is given by $E \simeq -20.8Z^{7/3}\text{eV}$, which is the exact result in the limit $Z \rightarrow \infty$. [8] This means that convincing arguments have been presented [8] that the Schrodinger equation for Z electrons in the coulombian field of the neutralizing atomic nucleus gives the ground-state energy $E \simeq -20.8Z^{7/3}\text{eV}$ in the limit $Z \rightarrow \infty$. Corrections have been brought to this result, the binding energy being represented as an asymptotic series in powers of $Z^{-1/3}$; this series includes, beside the leading term $-20.8Z^{7/3}\text{eV}$, the so-called "boundary correction" $13.6Z^2\text{eV}$, [9, 10] the exchange contribution $-5.98Z^{5/3}\text{eV}$ (or $-7.3Z^{5/3}\text{eV}$), [11] etc; in addition, the relativistic effects must also be considered for large Z .

In principle, such an asymptotic series should reproduce satisfactorily the experimental atomic binding energies; this would be an illustration of the "unreasonable utility of asymptotic estimates". [12] In fact, the empirical binding energy of heavy atoms is well represented by $E \simeq -16Z^{7/3}\text{eV}$ (see, for instance Ref. [9] and references quoted therein), which differs appreciably from the leading term of the asymptotic series.

In order to improve the results various computations have been worked out, including higher-order corrections to the quasi-classical approximation, self-consistent Hartree, or Hartree-Fock equations, as well as density-functional models. [13]-[15] At the same time, the Thomas-Fermi model revealed another drawback: it does not bind atoms in molecules. [16, 17]

We present here a different approach to the problem, which provides a more direct access to the $E \simeq -16Z^{7/3}\text{eV}$ -representation of the "empirical" binding energies of the atoms, and may throw additional light upon the nature of the Thomas-Fermi model and the quasi-classical description. The method employed here is a variational treatment of a linearized version of the Thomas-Fermi model, as based on the quasi-classical description. In particular, it binds atoms in large clusters.

2. LINEARIZED THOMAS-FERMI MODEL [18]

According to the prescriptions of the quasi-classical approximation, equation (1) is valid as long as the potential φ varies slowly in space; consequently, the Fermi wavevector k_F has also a slow spatial variation, so one may linearize equation (1) by

substituting $2\bar{k}_F k_F$ for k_F^2 , where \bar{k}_F is viewed as a variational parameter, assumed to be constant in space, the whole spatial dependence being transferred upon the new variable k_F ; this substitution is justified for those spatial regions where \bar{k}_F and k_F are comparable in magnitude, and one can see easily that this is so for a moderate range of intermediate distances; it is precisely this range over which the most part of the electrons are localized in heavy atoms, so that one may expect to get a reasonable description by employing this linearization procedure. Alternatively, we may consider the interaction as a small perturbation and write equation (1) as $\frac{\hbar^2}{m} k_F \delta k_F - e \delta \varphi = 0$; here we replace k_F by \bar{k}_F , δk_F by k_F and $\delta \varphi$ by φ . As remarked before, it is worth noting that although the Coulomb potential is singular at the origin, it extends over a small region around the origin, due to the screening, which makes its effects suitable to be treated as a small perturbation. On the other side, the original dependence of the electron density on the 3/2-power of the potential φ , $n \sim \varphi^{3/2} \sim 1/r^{3/2}$, overestimates the density in the zone of the abrupt variation of the potential φ , *i.e.* near the nucleus, where the potential goes like $\varphi \sim Ze/r$, in comparison with the linearized version $n \sim \varphi \sim 1/r$, which is contrary to the requirements of the quasi-classical approximation. We get $k_F = (me/\hbar^2 \bar{k}_F) \varphi$ for the linearized version of equation (1). A similar linearization for the electron density $n = k_F^3/3\pi^2 \rightarrow n = \bar{k}_F^2 k_F/\pi^2$ leads to $n = (me\bar{k}_F/\pi^2 \hbar^2) \varphi = (q^2/4\pi e) \varphi$, where the Thomas-Fermi screening wavevector q has been introduced through $q^2 = 4me^2 \bar{k}_F/\pi \hbar^2 = 4\bar{k}_F/\pi a_H$ (here $a_H = \hbar^2/me^2 \simeq 0.53\text{\AA}$ is the Bohr radius). Now, Poisson's equation (2) has the well-known solution $\varphi = (Ze/r)e^{-qr}$, *i.e.* the screened Coulomb potential, as expected. One can see that this potential falls abruptly to zero at large distance, where the quasi-classical description does not apply (as the wavelengths increase indefinitely there), varies slowly over intermediate distances, as expected, and has an abrupt variation over short distances, *i.e.* near the atomic nucleus; in the small region around the nucleus the computations will be corrected, as required by the quantum behaviour of the electrons in this region. For the moment, however, we proceed further on, by computing the total energy.

By using the same linearization procedure the kinetic energy $E_{kin} = V \hbar^2 k_F^5/10\pi^2 m$ of the electron gas enclosed in a volume V is replaced by

$$E_{kin} = (\hbar^2 \bar{k}_F^4/2\pi^2 m) \int d\mathbf{r} \cdot k_F = \frac{\pi e a_H^3}{128} q^6 \int d\mathbf{r} \cdot \varphi, \quad (3)$$

which yields $E_{kin} = \pi^2 a_H^3 Z e^2 q^4/32$. The potential energy is given by

$$\begin{aligned} E_{pot} &= \int d\mathbf{r} (\rho_e \varphi - \frac{1}{2} \rho_e \varphi_e) = \frac{1}{2} \int d\mathbf{r} (\rho_e \varphi + \rho_e \varphi_e) = \\ &= -\frac{e}{2} \int d\mathbf{r} n (\varphi + \varphi_e) = -\frac{q^2}{8\pi} \int d\mathbf{r} (\varphi^2 + \varphi \varphi_e), \end{aligned} \quad (4)$$

where $\rho_e = -en$ is the density of the electronic charge, $\varphi_e = \varphi - \varphi_c$ is the electric

potential produced by the electrons, and $\varphi_c = Ze/r$ is the Coulomb potential of the atomic nucleus. The computations are straightforward, and one obtains $E_{pot} = -3Z^2e^2q/4$. Therefore, the total energy reads

$$E = E_{kin} + E_{pot} = \frac{\pi^2 a_H^3}{32} Z e^2 q^4 - \frac{3}{4} Z^2 e^2 q, \quad (5)$$

which reaches the minimum value

$$E = -\frac{9 \cdot 6^{1/3}}{16\pi^{2/3}} Z^{7/3} \frac{e^2}{a_H} = -0.42 Z^{7/3} \frac{e^2}{a_H} = -11.4 Z^{7/3} eV \quad (6)$$

for the optimal value

$$q = (6/\pi^2)^{1/3} \frac{Z^{1/3}}{a_H} = 0.85 \frac{Z^{1/3}}{a_H} \quad (7)$$

of the variational parameter q ; we note the occurrence of the atomic unit for energy $e^2/a_H \simeq 27.2eV$ (another useful formula is $E = -(9/16)Z^2e^2q$, where q is given by equation (7)). (It is worth noting that the potential computed by solving numerically the 3/2-equation goes, approximately, like $\varphi \simeq (Ze/r)e^{-2qr}$ for $r \simeq 0$, where q is given by equation (7) (see, for instance, Ref. [5]); that means that it is more abrupt near the nucleus than the potential given by the linearized version, which is a consequence of the overstimulation of the electron density in the vicinity of the nucleus. This leads to an enhanced binding energy ($-20.8Z^{7/3}eV$). One can see that the radial density of electrons $\sim r^2n$, as given by $n = (q^2/4\pi e)\varphi$, has a maximum value for $R \sim 1/q \sim Z^{-1/3}a_H$, which may be taken as the "radius" of the electronic charge (while the "radius" of the atom is of the order of a_H); thus, one can see again that the quasi-classical description for large Z is justified; indeed, the quasi-classical description holds for distances longer than the radius a_H/Z of the first Bohr orbit and shorter than the Bohr radius a_H , and the electronic "radius" $R \sim Z^{-1/3}a_H$ is such that the inequalities $a_H/Z \ll R \sim a_H/Z^{1/3} \ll a_H$ are satisfied for large Z ; the most part of the electrons are localized around R , which justifies the statistical character of the Thomas-Fermi model 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 alters the distinction between the exact kinetic and potential energies, lead to the breakdown of the virial theorem; indeed, one can check easily that $E_{kin} = -(1/4)E_{pot}$, instead of $E_{kin} = -(1/2)E_{pot}$, as required by the virial theorem; this is not a major drawback, as it is well-known that approximate calculations may give wrong values for both the "kinetic" and "potential" energies and still the total energy be quite close to the exact one;[19] this is due to the variational treatment employed here.

3. QUANTUM CORRECTION

According to equation (1) and the Thomas-Fermi model, the electronic states are described by quasi-plane waves everywhere in space, their wavevector depending weakly on position; they correspond to the electron motion in a slowly-varying potential, vanishing at large distances; the screened Coulomb potential φ is consistent with this assumption, except for short distances where it has a sudden variation; the electron single-particle energies must therefore be corrected for this additional potential energy, corresponding to the electron motion close to the atomic nucleus; the correction is carried out to the first order of the perturbation theory, by estimating the average of the potential energy $-e\varphi$ over plane waves confined to a small spherical region of radius R around the nucleus; the radius R must be regarded as a variational parameter, and the correction to the energy will be minimized with respect to R ; doing so, we obtain an additional energy

$$-\frac{e}{v} \int_v d\mathbf{r} \cdot \varphi = -3Ze^2q \cdot \frac{1}{x^3} (1 - e^{-x} - xe^{-x}) \quad , \quad (8)$$

to each electron 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 $\int_v d\mathbf{r} \cdot n$; (the error made by counting twice the interacting part of this energy (Koopmans' factor 1/2) is $Z^2e^2q(1 + e^{-2x} - 2e^{-x})/4 \simeq 0.07Z^2e^2q$, and it can be neglected at this level of accuracy); one obtains

$$\Delta E = -3Z^2e^2q \cdot \frac{1}{x^3} (1 - e^{-x} - xe^{-x})^2 = \frac{16}{3}E \cdot \frac{1}{x^3} (1 - e^{-x} - xe^{-x})^2 \quad ; \quad (9)$$

this is a contribution to the total energy of the electrons, and it must be minimized with respect to the parameter R , or, equivalently, x , as noted above; the function of x in equation (9) has a maximum value 0.073 for $x \simeq 0.75$, which corresponds to $R \simeq Z^{-1/3}a_H$, *i.e.* close to the electronic "radius", and yields

$$\Delta E = 0.39E = -4.44Z^{7/3}\text{eV} \quad ; \quad (10)$$

therefore, the total energy is obtained as

$$E = -11.4Z^{7/3}\text{eV} - 4.44Z^{7/3}\text{eV} = -15.84Z^{7/3}\text{eV} \quad , \quad (11)$$

which agrees well with the "empirical" binding energy $E \simeq -16Z^{7/3}\text{eV}$. Since the values derived here for the variational and the electronic "radii" are close to each other one may say that the computations are consistent; one can see also that ΔE amounts to cca 28% of the binding energy E , so that one may indeed regard ΔE as a correction to this energy; higher-order perturbation theory calculations modify the electronic (quasi-) plane waves, and the single-particle energies, according to the quantum behaviour; however, according to the perturbation theory, the main contribution to the total energy given above is not affected significantly. It is worth noting

that the quantum correction given above vanishes in the limit $Z \rightarrow \infty$, as the electrons approach the quasi-classical limit; in addition, the main contribution $-11.4Z^{7/3}\text{eV}$ to the total energy derived above is in error in the limit $Z \rightarrow \infty$, as the linearization procedure is not valid anymore in this limit; indeed, the linearization holds as long as the Fermi wavevector k_F varies slowly in space; a measure of the departure from this behaviour is given by the extent to which the variational parameter $q = 0.85Z^{1/3}/a_H$ given by equation (7) differs from the parameter $q = (8Z/\pi^2)^{1/3}/a_H \simeq 0.9Z^{1/3}/a_H$ obtained from $q^2 = 4me^2\bar{k}_F/\pi\hbar^2 = 4\bar{k}_F/\pi a_H$, where the average \bar{k}_F is computed by using the electron density $n(\mathbf{r}) = (q^2/4\pi e)\varphi(r) = (q^2Z/4\pi)e^{-qr}/r$ derived here; as one can see, the difference in the q -values is $\sim 5\%$, which implies a similar decrease in the total energy from $-15.84Z^{7/3}\text{eV}$ to $-16.64Z^{7/3}\text{eV}$; this value has the tendency to be more negative (towards the exact value $-20.8Z^{7/3}\text{eV}$) for large Z , as it ought to be. For finite values of Z the error in energy produced by the linearization procedure is nearly compensated by the variational treatment of the quantum correction ΔE . This may explain the rather surprising proximity of the energy E given by equation (11) to the experimental atomic binding energy. In this regard, one may say that the present linearized Thomas-Fermi approach is more appropriate for an intermediate range of Z -values, as corresponding to the "actual" atoms. The exchange energy must be added to the result given above by equation (11), and one can check that it brings a $\sim 4\%$ -correction at most, for $Z = 20$. As it can be seen easily, the ΔE -correction computed here in equation (10) corresponds to the Hartree contribution to the linearized Thomas-Fermi model; a similar correction to the exchange energy can also be obtained; though very small, we give it here since such corrections have previously been discussed to a rather large extent, in the framework of the atomic theory; [11, 20] on the other hand, the computation of such exchange corrections helps to further enlighten the virtues of the linearized Thomas-Fermi model.

4. EXCHANGE ENERGY

As it is well known the exchange energy of a homogeneous gas of electrons is given by $E_{ex} = -(e^2/4\pi^3)Vk_F^4$; according to the linearization procedure this energy is written as

$$E_{ex} = -\frac{e^2}{\pi^3}\bar{k}_F^3 \int d\mathbf{r} \cdot k_F, \quad (12)$$

and making use of the results obtained above, in particular $n = \bar{k}_F^2 k_F/\pi^2$ and $n = (q^2/4\pi e)\varphi$ and the variational parameter q derived in equation (7), one obtains $E_{ex} = -18.12Z^{5/3}\text{eV}$. The correction to this exchange energy originates in the abrupt variation of the electronic density near the atomic nucleus; to the first-order of the per-

turbation theory it may be written as

$$\Delta E_{ex} = -\frac{e^2}{(2\pi)^6} \int_v d\mathbf{r} \int d\mathbf{r}' \int_F d\mathbf{k} d\mathbf{k}' \cdot e^{-i\mathbf{Q}\rho} \frac{1}{\rho}, \quad (13)$$

where $\mathbf{Q} = \mathbf{k} - \mathbf{k}'$, $\rho = \mathbf{r} - \mathbf{r}'$, v is the spherical volume of radius R around the nucleus, and F denotes the Fermi sea; in contrast to the Hartree correction given by equation (9), the integration over \mathbf{r}' is extended over the whole space, as a consequence of the non-local character of the exchange energy. The calculations in equation (13) proceeds in the usual manner; first, we pass from the integration over \mathbf{r}' to the integration over ρ ; the result of this integration is $4\pi/Q^2 - (4\pi/3)r(3R+2r) + \dots$; one may neglect the small contribution of the second term, and retain the main term $4\pi/Q^2$; next, we perform the \mathbf{k}, \mathbf{k}' -integrations, which lead to

$$\Delta E_{ex} = -\frac{e^2}{4\pi^3} \int_v d\mathbf{r} \cdot k_F^4; \quad (14)$$

according to the linearization procedure equation (14) may also be written as

$$\Delta E_{ex} = -\frac{e^2}{\pi^3} \bar{k}_F^3 \int_v d\mathbf{r} \cdot k_F; \quad (15)$$

one gets straightforwardly $\Delta E_{ex} = (1 - e^{-x} - xe^{-x})E_{ex}$, where E_{ex} is given by equation (12) and $x = qR$; for the electronic "radius" $x \simeq 1$ one obtains $\Delta E_{ex} \simeq 0.27E_{ex}$, while for the variational "radius" $x \simeq 0.85$ derived above one obtains $\Delta E_{ex} \simeq 0.21E_{ex}$; it follows that the exchange energy changes by a factor which lies somewhere between 1.21 and 1.27; it agrees well with similar exchange corrections derived in Ref. [11] (which indicates a factor 1.22). It is customary to refer such a factor in the exchange energy, denoted by α , to the value $2/3$, which corresponds to the homogenous electron gas, *i.e.* to E_{ex} in the present calculations (and which is known as the Kohn-Sham value [21, 22]); this is the α -factor in Slater's $X\alpha$ -method (and in density-functional calculations);[20] according to the present results the value of the α -factor runs between $\alpha \simeq (2/3) \cdot 1.21 \simeq 0.8$ and $\alpha \simeq (2/3) \cdot 1.27 \simeq 0.85$; more accurate density-functional computations [20],[23, 24] of atomic and molecular orbitals recommend $\alpha \simeq 0.69 - 0.75$, which are in good agreement with the present results (the terms neglected in the above ρ -integration diminish to some extent the value of the α -factor); while Slater's original value [25] is $\alpha = 1$.

5. GIANT DIPOLE OSCILLATIONS

The electrons may move as a whole with respect to the nucleus under the action of an external electric field; for an oscillating external field the electrons may perform giant dipole oscillations. During such small oscillations the equilibrium is preserved,

such as $Rq = \text{const}$; consequently, the small displacement $u = \delta R$ is related to the change δq in the screening wavevector q by $u = (1/q^2)\delta q$. It follows that the change in the energy arises solely from the change in the kinetic energy, given in equation (5); we get

$$\delta E = \delta E_{kin} = \frac{27}{4\pi^2} \frac{Z^3 e^2}{a_H^3} u^2; \quad (16)$$

this energy corresponds to a frequency ω_0 given by $\delta E = \frac{1}{2} M \omega_0^2 u^2$, where $M = Zm$ is the mass of all the electrons; we get the frequency

$$\omega_0 = \left(\frac{27}{2\pi^2} \right)^{1/2} \frac{Ze}{\sqrt{ma_H^3}} \simeq 4.5Z \times 10^{16} s^{-1}; \quad (17)$$

it corresponds to an energy $\hbar\omega_0 \simeq 28ZeV$, which is in the range of moderate X-rays. The wavelength $\lambda_0 = 2\pi c/\omega_0 \simeq \frac{4.2}{Z} \times 10^{-6} cm$ is still much longer than the dimension of the atom ($c = 3 \times 10^{10} cm/s$ is the speed of light). This is consistent with our adiabatic hypothesis that during oscillations the equilibrium is preserved ($e = 4.8 \times 10^{-10} \text{ statcoulomb}$, $m = 10^{-27} g$, $\hbar = 10^{-27} \text{ erg} \cdot s$).

As it is well known, an oscillating dipole radiates energy; consequently, a damping force acts upon the dipole, given by $F_d = 2Q^2\ddot{v}/3c^3$, where $Q = -Ze$ is the charge of all the electrons and v is the velocity of the dipole; for the external frequency ω close to the eigenfrequency ω_0 , we may put $\ddot{v} = \omega_0^2 v$ and write

$$F_d = \frac{2Z^2 e^2}{3c^3} \omega_0^2 v = M\gamma\dot{u}, \quad (18)$$

where

$$\gamma = \frac{2Ze^2}{3mc^3} \omega_0^2 \quad (19)$$

is a damping coefficient. We note that $\gamma \ll \omega_0$, since $2Ze^2/3mc^2 \ll c/\omega_0$, where $e^2/mc^2 = r_0 \simeq 2.8 \times 10^{-13} cm$ is the classical electromagnetic radius of the electron ($c = 3 \times 10^{10} cm/s$). The quality ratio (natural breadth of the spectroscopic line) is

$$\frac{\gamma}{\omega_0} = \frac{4\pi Z r_0}{3\lambda_0} \simeq 2.8Z^2 \times 10^{-7}. \quad (20)$$

Putting together all this information we can write the equation of motion for the electrons

$$M\ddot{u} + M\omega_0^2 u + M\gamma\dot{u} = QE \cos \omega t, \quad (21)$$

or

$$m\ddot{u} + m\omega_0^2 u + m\gamma\dot{u} = -eE \cos \omega t, \quad (22)$$

where E is the external electric field. We do not include the effects of the magnetic field since the ratio v/c is very small, as we can see easily by comparing the kinetic energy with Mc^2 . Since the wavelength is much longer than the dimension of the

atom (quasi-stationary regime) we should include the effect of the internal (polarization) field; we do not, since this field is valid only for macroscopic bodies (or bodies with a definite surface). The (particular) solution of equation (22) is

$$u = a \cos \omega t + b \sin \omega t, \quad (23)$$

where

$$a = \frac{eE}{m} \frac{\omega^2 - \omega_0^2}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2}, \quad b = -\frac{eE}{m} \frac{\omega \gamma}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2}. \quad (24)$$

We can see that the electrons perform giant dipole oscillations with characteristic frequency (eigenfrequency) ω_0 . From the energy conservation in equation (22) we get the power loss

$$P = m \gamma \overline{\dot{u}^2} = \frac{e^2 E^2}{2m} \frac{\gamma \omega^2}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2}, \quad (25)$$

which, at resonance, becomes $P_{res} = e^2 E^2 / 2m\gamma$. Making use of equations (17) and (20), for moderate fields $E = 1/300 \text{ statvolt/cm}$ (100 V/m) we get a power loss

$$P_{res} = \frac{1}{Z^3} \times 10^{-7} \text{ erg/s}; \quad (26)$$

it corresponds to a transition rate

$$R = P_{res} / \hbar \omega_0 \simeq \frac{2}{Z^4} \times 10^3 \text{ s}^{-1}, \quad (27)$$

where R represents the number of elementary acts of oscillation per unit time. The formula given by equation (25) is valid for one electron; for the atom we must multiply equation (25) by Z . The transition rate remains unchanged, because each electron is an oscillator which absorbs (and emits) an energy quanta $\hbar \omega$ ($\hbar \omega_0$).

The linearized Thomas-Fermi model allows the estimation of a motion involving only $1 \ll \delta Z < Z$ electrons, the rest of $Z - \delta Z$ electrons together with the atomic nucleus being considered as an inert core with charge $\delta Z \cdot e$. The characteristic frequency given by equation (17) becomes $(\delta Z / Z) \omega_0$ and the damping coefficient is $(2e^2 \delta Z / 3mc^3) \omega_0'^2$.

6. ANHARMONICITIES AND IONIZATION

It is worth estimating the amplitude of oscillations, which, at resonance, is given by

$$|b_0| = \frac{eE}{m\omega_0\gamma} = \frac{8}{Z^4} \times 10^{-10} E \text{ cm}, \quad (28)$$

from equations (17), (20) and (23). For an extended range of field intensities this amplitude is much smaller than the characteristic distances in atom, for instance,

the Bohr radius. Consequently, the harmonic approximation is justified. Higher-order corrections to the harmonic approximation are obtained by including higher-order terms in the kinetic energy given in equation (5) and using the relationship $(q + \delta q)(R + u) = 1$ ($\delta q = -q^2 u / (1 + qu)$), which corresponds to the adiabatic perturbation, valid as long as the oscillation frequency is much smaller than the frequency of the quantum one-particle state. We get a potential energy

$$U = \frac{1}{2} M \omega_0^2 u^2 \left(1 - \frac{8}{3} q u + \frac{31}{6} q^2 u^2 + \dots \right), \quad q = (6/\pi^2)^{1/3} Z^{1/3} / a_H = 0.85 Z^{1/3} / a_H, \quad (29)$$

which contains anharmonic terms. As it is well known, the corresponding non-linear (free) oscillations imply higher-order harmonics (with frequencies $2\omega_0$, $3\omega_0$, etc), displacements of the equilibrium position and shifts in the original frequency ω_0 , which may be computed either by successive approximations or by the self-consistent harmonic-oscillator approximation. In particular, the frequency shifts are worth noting, since they determine abrupt changes in the oscillation amplitude near resonance ($\omega \simeq \omega_0$); due to the combined frequencies phenomenon, the ω_0 -resonance may be excited by other frequencies, or other resonances may be excited.[26]

Since $\delta q = -q^2 u / (1 + qu)$, for large oscillation amplitudes ($u \rightarrow \infty$) we get the energy $U_\infty = 9Z^2 e^2 q / 16$ (with $q = 0.85 Z^{1/3} / a_H$); this energy cancels out exactly the binding energy given by equation (6), as expected, setting the electrons free (the quantum energy correction is vanishing in this limit). Therefore, in order to have complete ionization (hyper-ionization, dissociation) we should compare the amplitude given by equation (28) with the Bohr radius; we get

$$E > 7Z^4; \quad (30)$$

this is a high field, for (*X*-ray) frequency ω_0 . (High-intensity fields are generated in short laser pulses; for instance, for intensity $I = 10^{15} w/cm^2$ we get an electric field $E = 10^6 \text{ statvolt/cm}$ ($E \simeq \sqrt{I/c}$); this is an "atomic field", of the order of the electron field in atoms; it may generate ionization and high-order harmonics. For intensities $10^{19} w/cm^2$ (current intensities) the field is of the order 10^8 statvolt/cm , where relativistic and non-linear effects appear; for ultrahigh intensities $10^{21} w/cm^2$ the field is 10^9 statvolt/cm , where multi-photon processes appear, the structure of the quantum vacuum may also occur, as well as particle production (the Schwinger field, which indicates a limit of quantum electrodynamics calculations, is $10^{13} \text{ statvolt/cm}$). All these fields are optical fields (energy $\simeq 1 \text{ eV}$, frequency $\simeq 10^{15} s^{-1}$, wavelength $\simeq 10^{-4} \text{ cm} = 1 \mu\text{m}$); typically, the pulse duration is 50 fs ($1 \text{ fs} = 10^{-15} \text{ s}$) and the pulse dimension is $d \simeq 15 \mu\text{m}$; for intensity $10^{21} w/cm^2$ the power is $P \simeq 1 \text{ pw}$ ($1 \text{ p} = 10^{15}$).). For the motion of a fraction δZ of electrons ($1 \ll \delta Z < Z$) we have $\omega_0 = 4.5 \delta Z \times 10^{16} s^{-1}$ and $\gamma/\omega_0 = 2.8(\delta Z)^2 \times 10^{-7}$. We can see that ω_0 may lie now in the ultraviolet range. $\hbar\omega_0$ can be viewed as an ionization

energy; for $\delta Z = 1$ we get $\hbar\omega_0 = 30eV$, which is higher than the (first) ionization potential of the elements (an average of $6eV$); we note that the extrapolation to $\delta Z = 1$ is not permissible. The critical electric field for partial ionization is given by

$$E > 7(\delta Z)^4, \quad (31)$$

which is much smaller than the field for total ionization given by equation (30).

7. QUASI-CLASSICAL APPROXIMATION

As it is well known, the equation of motion for an operator O reads $\dot{O} = \frac{i}{\hbar}[H, O]$, or $\dot{O}_{mn} = \frac{i}{\hbar}(E_m - E_n)O_{mn} = i\omega_{mn}O_{mn}$, where H is the Hamiltonian, E_n , E_m are the energies of the states n and, respectively, m and $\omega_{mn} = (E_m - E_n)/\hbar$ is the frequency of transition between the states n and m . In the quasi-classical approximation the quantum states are sufficiently dense to approximate the frequency ω_{mn} by $\omega_{mn} \simeq -s(\partial E_m/\partial m)_m = -\omega_s$, where $n = m + s$ and E_n depends slightly on n in the vicinity of m ; this amounts to a quasi-classical motion which implies a mechanical action much greater than \hbar . Similarly, for a set of quantum states sufficiently dense the matrix elements $O_{mn} = O_{m,m+s}$ depends slightly on s for small s , and vanishes rapidly for greater s , so that we may write $O_{mn} = O_{m,m+s} \simeq O_s$; in fact, O_s is the temporal Fourier transform of O , corresponding to the frequency ω_s ; (the average of O with the wavefunction $\psi = \sum_n c_n \varphi_n e^{-i\omega_n t}$ is $\bar{O} = \sum_{mn} c_m^* c_n O_{mn} e^{i\omega_{mn} t} = \sum_{ms} c_m^* c_{m+s} O_{m,m+s} e^{-i\omega_s t}$, which is approximately $\bar{O} \simeq \sum_m |c_m|^2 \sum_s O_s e^{-i\omega_s t} \simeq \sum_s O_s e^{-i\omega_s t}$; $O_s(t) = O_s e^{-i\omega_s t}$ is the time-dependent operator in the quasi-classical equation of motion (32)); we may drop out the label s of the O_s , and we may add an external force, as represented by a Hamiltonian h , in general time-dependent; the equation of motion becomes $\dot{O} = -i\omega_s O + (\partial O^{cl}/\partial t)_{cl;h}$, where the last term means the time derivative of the classical counterpart O^{cl} of O , as given by h , according to the classical motion. With $O = O^{(1)} + iO^{(2)}$, we get $\dot{O}^{(1)} = \omega_s O^{(2)} + (\partial O^{cl}/\partial t)_{cl;h}$, $\dot{O}^{(2)} = -\omega_s O^{(1)}$ (since the classical quantity $(\partial O^{cl}/\partial t)_{cl;h}$ is real); we get $\ddot{O}^{(1)} + \omega_s^2 O^{(1)} = (\partial/\partial t)(\partial O^{cl}/\partial t)_{cl;h}$; here, we may identify $O^{(1)}$ with the time-dependent part of the classical quantity O^{cl} , and leave aside the labels (similarly for $O^{(2)}$); (the general solution for $O^{(1)}$ from the homogeneous version of equation (32) is $O^{(1)} = A \cos(\omega_s t + \delta)$, where A is amplitude and δ is a phase, both undetermined; from $\dot{O}^{(2)} = -\omega_s O^{(1)}$, we get $O^{(2)} = -A \sin(\omega_s t + \delta)$, and $O = O^{(1)} + iO^{(2)} = A e^{-i(\omega_s t + \delta)}$, as expected; the latter ($\sim e^{-i\omega_s t}$, or $e^{i\omega_s t}$) is the quantum version (in the quasi-classical approximation), while the former ($\sim \cos \omega_s t$, or $\sin \omega_s t$) is the classical version of the same quantity); we get

$$\ddot{O} + \omega_s^2 O = (\partial/\partial t)(\partial O^{cl}/\partial t)_{cl;h} = f; \quad (32)$$

this is the equation of motion of a classical harmonic oscillator subjected to the action of a classical force f ; (the force f should contain only c -numbers (if necessary, they can be determined by comparing the absorbed power computed both classically and quantum-mechanically); its eigenfrequency ω_s is the quantum transition frequency ω_{mn} in the quasi-classical approximation. Since the approximation is valid for a wavepacket, we may also introduce a lifetime γ^{-1} given by a damping term $\gamma\dot{O}$ in equation (32).

The "peripheral" electrons in atom, *i.e.* the electrons with high quantum numbers (and high energy) in the mean-field atomic potential, which may be subjected to ionization by the action of an (optical) electromagnetic field, satisfy the conditions for the quasi-classical approximation in heavy atoms; under the action of the Hamiltonian $\hat{h} = eEu \cos\omega t$, force $f = -eE \cos\omega t$, where E is the electric field and u is the displacement, the equation of motion of such an electron is

$$\ddot{u} + \omega_0^2 u + \gamma \dot{u} = -\frac{e}{m} E \cos\omega t, \quad (33)$$

where $\omega_0 (= \omega_s)$ is the ionization frequency (excited states are described similarly). The amplitude at resonance is given by $|b_0| = eE/m\omega_0\gamma$ (equation (28)), where the damping coefficient is $\gamma = 2r_0\omega_0^2/3c = 6 \times 10^{-24}\omega_0^2$ (equation (19)). We take $\omega_0 = 10^{16} s^{-1}$ ($\hbar\omega_0 = 6eV$, average ionization potential) and get $|b_0| = 10^{-7} E cm$; compared with the Bohr radius, it leads to a critical field of ionization $E > 5 \times 10^{-2} statvolt/cm$ ($\simeq 1500V/m$). For higher fields we may have multiple-quanta transitions; they correspond to larger displacements for an oscillator, when the harmonic approximation does not hold anymore. The mean-field potential U which gives $\omega_0^2 = (1/m)(\partial^2 U/\partial u^2)_0$ may contribute now higher-order terms like $\sim u^3$, $\sim u^4$, which leads to anharmonicities in the classical equation of motion (33).

8. CONCLUSION

In conclusion, one may say that the variational treatment of the linearized Thomas-Fermi model provides a consistent quasi-classical description for the atomic binding energies in the range of realistic values of atomic numbers Z (heavy atoms), provided the quantum corrections (Hartree-type contributions) are properly included. (This might be expected since the "boundary effect" included in the asymptotic series originates in the quantum corrections too (see, for instance, Refs. [9] and [10], and discussion therein)). Making use of the Thomas-Fermi model it was shown here that giant dipole oscillations may be induced in heavy atoms by external electromagnetic fields in the moderate X -ray range, which may lead to the ionization in intense fields. Frequency shifts and higher-order harmonics can be produced by anharmonicities in the dipole oscillations. Quasi-classical equation of motion for "peripheral"

electrons was also derived (a harmonic-oscillator equation), which can be used for investigating transitions to excited states or ionization in heavy atoms.

APPENDIX

A. EXCHANGE ENERGY

The exchange energy of a set of electrons which interact through the Coulomb potential (the Fock term) is given by

$$E_{ex} = -\frac{e^2}{2V^2} \int d\mathbf{r} d\mathbf{r}' \sum_{\mathbf{k}\mathbf{k}'(\uparrow\uparrow)} \frac{\varphi_{\mathbf{k}'}^*(\mathbf{r}')\varphi_{\mathbf{k}}(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|} \varphi_{\mathbf{k}}^*(\mathbf{r})\varphi_{\mathbf{k}'}(\mathbf{r}), \quad (34)$$

where $-e$ is the electron charge, V is the volume enclosing the set of electrons, $\varphi_{\mathbf{k}}(\mathbf{r})$ are the single-particle wavefunctions and the summation includes parallel spins; the summation over \mathbf{k}, \mathbf{k}' is performed over the Fermi sea. For plane waves $\varphi_{\mathbf{k}}(\mathbf{r}) = e^{i\mathbf{k}\mathbf{r}}$ we get

$$E_{ex} = -\frac{e^2}{V} \sum_{\mathbf{k}\mathbf{k}'} \int d\mathbf{r} \frac{e^{i\mathbf{q}\mathbf{r}}}{r}, \quad (35)$$

where $\mathbf{q} = \mathbf{k} - \mathbf{k}'$. The Fourier transform of the Coulomb potential is $\int d\mathbf{r} e^{i\mathbf{q}\mathbf{r}}/r = 4\pi/q^2$, so the exchange energy becomes

$$E_{ex} = -\frac{2e^2}{(2\pi)^5} V \int d\mathbf{k} d\mathbf{k}' \frac{1}{q^2}. \quad (36)$$

We introduce the new variables $\mathbf{q} = \mathbf{k} - \mathbf{k}'$ and $\mathbf{p} = \mathbf{k} + \mathbf{k}'/2$; it is easy to see that the integration over \mathbf{p} extends over the intersection of two Fermi seas separated by \mathbf{q} , $0 < q < 2k_F$, where k_F is the Fermi wavevector. This intersection consists of two equal spherical sectors, subtended by the angle θ_0 given by $\cos\theta_0 = q/2k_F$. The volume of a spherical sector is

$$v = \int \pi k_F^2 \sin^2\theta \cdot k_F d\theta \sin\theta = \frac{2\pi}{3} k_F^3 \left(1 - \frac{3}{2} \cos\theta_0 + \frac{1}{2} \cos^3\theta_0\right). \quad (37)$$

We get the exchange energy

$$E_{ex} = -\frac{8e^2}{3(2\pi)^3} V k_F^3 \int_0^{2k_F} dq \left(1 - \frac{3}{2} \frac{q}{2k_F} + \frac{1}{2} \frac{q^3}{(2k_F)^3}\right) = -\frac{e^2}{4\pi^3} V k_F^4. \quad (38)$$

It is usual to introduce the inter-particle separation r_s through $n = k_F^3/3\pi^2 = 1/(4\pi r_s^3/3)$, *i.e.* $k_F r_s = (9\pi/4)^{1/3}$; the exchange energy per electron is written as

$$E_{ex}/N = -\frac{e^2}{2a_H} \frac{2}{3\pi^2} \left(\frac{9\pi}{4}\right)^{4/3} \frac{1}{r_s} = -\frac{0.916}{r_s} r_y, \quad (39)$$

where N is the number of electrons, r_s is measured in Bohr radii ($a_H = \hbar^2/m_e^2 = 0.53\text{\AA}$) and the energy is measured in rydbergs ($1ry = e^2/2a_H = 13.6eV$). Similarly, the kinetic energy leads to $E_{kin}/N = 2.21/r_s^2ry$ (next-order contributions to the perturbation series, which give the correlation energy, are $0.062 \ln r_s - 0.094$).[27]

B. KOOPMANS' FACTOR

We may have an estimation of the effect of the Koopman's factor 1/2 by comparing the energy correction

$$\Delta E = \int_v d\mathbf{r} \rho_e \varphi = -Z^2 e^2 q^2 \int_0^R dr e^{-2qr} = -\frac{1}{2} Z^2 e^2 q (1 - e^{-2qR}) \quad (40)$$

with

$$\Delta E' = \int_v d\mathbf{r} (\rho_e \varphi - \frac{1}{2} \rho_e \varphi_e) = \frac{1}{2} \int_v d\mathbf{r} \rho_e (\varphi + \varphi_c), \quad (41)$$

where $\rho_e = -en$ is the electron charge density, n is the electron density, $\varphi_e = \varphi - \varphi_c$ is the electron potential and $\varphi_c = Ze/r$ is the potential of the nucleus (core potential). We get

$$\Delta E' = -\frac{1}{4} Z^2 e^2 q (3 - e^{-2qR} - 2e^{-qR}) \quad (42)$$

and

$$\Delta E - \Delta E' = \frac{1}{4} Z^2 e^2 q (1 + e^{-2qR} - 2e^{-qR}), \quad (43)$$

which is indeed very small ($\simeq 0.07 Z^2 e^2 q$) for $qR = 0.75$.

In fact, Koopmans' factor does not appear in the energy correction given by equations (8) and (9) since the potential φ is mainly determined by electrons lying away from the nucleus, while the quantum correction implies electrons placed close to the nucleus; or, in other words, the quantum correction, which implies the strong variation of the potential φ , *i.e.* an appreciable deviation from the quasi-classical approximation, is determined mainly by the nucleus.

C. QUANTUM AND CLASSICAL TRANSITIONS

The quantum transition amplitude from state n to state k , energies E_k and, respectively, E_n , under the action of a perturbation $V(t) = V \cos \omega t$, in the first order of the perturbation theory, is given by

$$i\hbar \dot{c}_k = V_{kn}(t) e^{i\omega_{kn}t}, \quad (44)$$

or

$$c_{kn} = -\frac{i}{2\hbar} \int_{-\infty}^t dt' V_{kn} \left[e^{i(\omega + \omega_{kn})t + \alpha t'} + e^{i(-\omega + \omega_{kn})t + \alpha t'} \right], \quad (45)$$

where $\omega_{kn} = (E_k - E_n)/\hbar$ the interaction is introduced adiabatically ($\alpha \rightarrow 0^+$); we retain only transitions with $\omega > 0$, and get

$$c_k = \frac{V_{kn}}{2\hbar} \frac{e^{i(-\omega + \omega_{kn})t + \alpha t}}{\omega - \omega_{kn} + i\alpha}. \quad (46)$$

The transition rate (number of transitions per unit time) is given by

$$R = \frac{\partial |c_k|^2}{\partial t} = \frac{|V_{kn}|^2}{2\hbar^2} \frac{\alpha}{(\omega - \omega_{kn})^2 + \alpha^2} \rightarrow \frac{\pi |V_{kn}|^2}{2\hbar^2} \delta(\omega - \omega_{kn}). \quad (47)$$

For a dipolar interaction $V = eEu$ ($-\mathbf{dE}$, where d is the electric dipole moment) we get

$$R = \frac{e^2 E^2 |u_{kn}|^2}{2\hbar^2} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2}, \quad (48)$$

or, for $\omega_{kn} = \omega_0$ ("quantum" oscillations), $k = 1$, $n = 0$, $u_{10} = \sqrt{\hbar/2m\omega_0}$,

$$R = \frac{e^2 E^2}{4m\hbar\omega_0} \frac{\alpha}{(\omega - \omega_0)^2 + \alpha^2} \simeq \frac{e^2 E^2}{2m\hbar\omega_0} \frac{2\alpha\omega^2}{(\omega^2 - \omega_0^2)^2 + 4\omega^2\alpha^2}, \quad (49)$$

which coincides with equations (25) and (27) for classical oscillations ("classical transitions") for $\omega \simeq \omega_0$ and $2\alpha = \gamma$.

It may appear disagreeable that the same result is obtained for "quantum transitions", *i.e.* transitions from the ground-state to the first excited state of the oscillator, and the "classical transitions", *i.e.* oscillations of the classical oscillator. The explanation resides in the fact that the classical harmonic oscillator is restricted to small oscillations, which correspond in fact to quantum motion, while the quantum oscillator allows also large displacements, which may trespass the harmonic-oscillations criterion of small displacement (the matrix elements of the displacement x for a harmonic oscillator with frequency ω , mass m are $x_{n,n-1} = \sqrt{n\hbar/2m\omega}$). In this context, the quasi-classical approximation gives only the small variation of the quantum transitions.

D. DIPOLAR RADIATION

It is worth comparing the radiated intensity to the power loss. The radiation intensity (energy per unit time) is given by

$$I = \frac{2e^2}{3c^3} \ddot{u}^2 = \frac{1}{3} E^2 r_0^2 c \frac{\omega^4}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2} \quad (50)$$

for a dipole $-eu$. Making use of the power loss given by equation (25),

$$P = \frac{e^2 E^2}{2m} \frac{\gamma\omega^2}{(\omega^2 - \omega_0^2)^2 + \omega^2 \gamma^2}, \quad (51)$$

we get $I/P = 2r_0\omega^2/3c\gamma$. For $\omega = \omega_0$, making use of equation (19) (with $Z = 1$), we get $I = P$. The result does not depend on Z , such that it holds also for atom.

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