Quantum-statistical model of an atom with multiple vacancies

V. S. Marchenko

Kurchatov Atomic Energy Institute

(Submitted 30 January 1987)
Zh. Eksp. Teor. Fiz. 1616–1629 (November 1987)

The feasibility of using the Thomas-Fermi statistical model to describe x-ray or Auger spectra of atoms with multiple vacancies is investigated. It is proposed to determine the potential of a multivacancy atom by self-consistent system of equations in which a solution of the one-electron Schrödinger equations is needed only for shells containing vacancies. It is shown that the presence of vacancies can be taken into account in the statistical Thomas-Fermi model by introducing an external equivalent positive potential. Expressions are obtained for the total energy of a multivacancy atom. Specific calculations for the atoms Ne, Ar, Cu, and Mo with vacancies in the 1*s* and 2*p* shells agree well with the available Hartree-Fock and experimental spectroscopic data.

1. INTRODUCTION

Atoms and ions with multiple vacancies in the inner shells are usually obtained in ion-atom collisions with energies exceeding 1 MeV/amu (see, e.g., Ref. 1). An interesting method of obtaining multivacancy atoms was recently demonstrated in Ref. 2, where the surface of a metal was bombarded by multiply charged Ar^{17+} ions that recombined with the electrons of the metal. Multivacancy atoms are manifested for the most part by their x rays that usually undergo a short-wave shift, or by the spectra of the electrons produced when the vacancies are filled by Auger processes.

A theoretical description of the shift of x-rays and of Auger electrons in the presence of multiple vacancies in the atoms calls for complicated Hartree-Fock calculations. So far, only a limited number of calculations of this type (see, e.g., Refs. 3 and 6) exist for several elements. At the same time, as will be shown in the present paper, simplified calculations can be performed by using the statistical Thomas-Fermi (TF) method. Numerical solutions of the Schrödinger equation for various *nl* shells using TF or the TFD (Thomas-Fermi-Dirac) potentials usually (see, e.g., Refs. 7–11) fair approximations of the wave functions and binding energies of the electrons, and are frequently used as the zeroth approximation for Hartree-Fock equations, or for a simplified treatment of certain scattering problems. This approach has, however, a number of shortcomings. First, the density of the quantum electron is already contained in the total density of the statistical electrons, i.e., the "self-action" of the electron is taken in practice into account. Accordingly, the total TF potential used in the Schrödinger equation does not have the Coulomb asymptotic form at infinity, and the use of various matchings to the Coulomb potential (see, e.g., Refs. 7 and 8) is not sufficiently well founded. Second, this approach does not permit in principle to introduce vacancies in the shells and calculate the corresponding shifts of the x-ray and Auger spectra. Third, additional inaccuracies in the calculation of the term energies can result from the presence, near the nucleus, of an electron-density divergence determined with the aid of the TF method.

We propose here a method for a self-consistent solution of the Schrödinger equations for electrons of certain *nl* shells, in a quantum approach, and of the statistical TF equation for the remaining electrons, with allowance for the decrease of their density by the onset of vacancies. This method remains relatively simple compared with the Hartree-Fock method. On the other hand, it is self-consistent and free of the indicated shortcomings inherent in the direct use of the TF atom potential for quantum calculations. We note that attempts at a self-consistent treatment of quantum electrons and TF electrons were made earlier only in problems of a different kind,[12–14] involving the investigation of the screening of atomic quantum electrons by free plasma electrons. In the present paper we likewise consider in fact the problem of screening of quantum electrons, but a statistical rather than free gas of bound TF electrons. This leads to equations of another type and, furthermore, semiclassical introduction of the vacancies raises the question of the correct choice of the boundary E_0 between the quasicontinuous and discrete energy spectra. This problem does not arise for a gas of free electrons, and the boundary is the electron energy at an infinite distance from the considered atom ($E_0 = 0$). To determine the boundary energy E_0 for an atom it is necessary to write a supplementary equation that stems from the self-consistency conditions on the complete system of equations. Limiting the spectrum from below eliminates also the errors due to the presence of a divergence of the electron density of a TF gas in the region of the nucleus.

Two methods of introducing vacancies into the TF equation are considered. It is shown that the self-consistent system of equations turns out to be simpler when the vacancies are introduced by the quantum approach, but the semiclassical method ensures a more correct behavior of the statistical TF electrons in the region of the nucleus, and accordingly a higher accuracy of the calculated terms.

The actual calculations were carried out for the atoms Ne, Ar, Cu, and Mo (i.e., at $Z = 10, 18, 29, 42$) with introduction of vacancies in the 1*s* and 2*p* shell. The results accord well with the available Hartree-Fock calculations[6] for Ar ($Z = 18$) and permit the experimental[2] shifts and widths of the k_α and k_β lines of Ar to be qualitatively explained as being due to multiple vacancies.

2. BASIC EQUATIONS

A simplified description of a multivacancy atom can be obtained by dividing all the atomic electrons into quantum electrons and semiclassical ones describable in the statistical TF model. The total electron density ρ_Σ can be represented in this case as a sum of statistical $\rho_e(\mathbf{r})$ and quantum

0038-5646/87/110924-07$04.00

$$\rho_q(\mathbf{r}) = \sum_{nl} \xi_{nl} |\psi_{nl}|^2,$$

of the electrons, where ξ_{nl} is the number of electrons in a given shell (n and l are the principal and orbital quantum numbers), and ψ_{nl} is the wave function of the nl-shell electrons. For the total potential φ of the atom we can write the usual electrostatic equation:

$$\Delta\varphi = 4\pi\rho_\Sigma = 4\pi\rho_e(\mathbf{r}) + 4\pi \sum_{nl} \xi_{nl} |\psi_{nl}|^2, \tag{1}$$

which takes into account the interaction of the electrons with one another and their interaction with the nucleus (via the boundary condition as $r \to 0$). The summation in (1) is over all the shells that are described in the quantum approach. For most applications it can be assumed that the vacancies are concentrated predominantly in the inner shells $n < n_0$, while the higher levels $n \geqslant n_0$ contains no vacancies. It is accordingly advantageous to assume that the statistical electrons occupy the energy region from E_0 to E_F ($E_0 < E_F < 0$), where there are no vacancies, with the Fermi energy $E_F = 0$ for the case of neutral atoms, while E_0, the lower energy limit of the continuum electrons, will be determined below from the self-consistency condition on Eq. (1) and the Schrödinger equations for the shells $n \leqslant n_0$ (in the usual TF model of a vacancy-free atom one assumes $E_0 = -\infty$).

In the TF model with a bounded energy spectrum of the electrons $\varepsilon = -\varphi + p^2/2$ in the range $-|E_0| < \varepsilon < -|E_F|$, the connection between the electron density and the potential follows from the usual relations of quantum statistics:

$$\rho_e(\mathbf{r}) = \frac{2}{(2\pi)^3} \int_{E_0}^{E_F} 4\pi p^2 \, dp(E) = \frac{2^{1/2}}{\pi^2} \int_{E_0}^{E_F} (\varepsilon + \varphi)^{1/2} d\varepsilon$$
$$= \frac{2^{7/2}}{3\pi^2} [(\varphi + E_F)^{3/2} \theta(\varphi + E_F) - (\varphi + E_0)^{3/2} \theta(\varphi + E_0)]. \tag{2}$$

Here $\theta(x) = 1$ for $x \geqslant 0$ and $\theta(x) = 0$ for $x < 0$. Introducing the screening function $\chi = r(\varphi + E_F)/Z$ and substituting (2) in (1) we obtain

$$\chi'' = \frac{2^{7/2} r}{3\pi Z} \left[\frac{Z^{3/2}}{r^{3/2}} \chi^{3/2} \theta(\chi) - \left(\frac{Z\chi}{r} + E_0 - E_F \right)^{3/2} \theta(\varphi + E_0) \right]$$
$$+ \frac{4\pi r}{Z} \sum_{nl} \xi_{nl} |\psi_{nl}|^2, \tag{3}$$

where Z is the charge of the ion nucleus. Equation (3) must be supplemented by the Schrödinger equations for the quantum electrons that occupy the energy space $E < E_0$:

$$-{}^1/_2 \nabla^2 \psi_i + U(\mathbf{r}) \psi_i = E_i \psi_i,$$
$$U(\mathbf{r}) = -\varphi - V_i^e, \quad V_i^e = -\int \frac{\psi_i^2 \, d\mathbf{r}'}{|\mathbf{r} - \mathbf{r}'|}. \tag{4}$$

Here $U(\mathbf{r})$ is the potential for the quantum electron of the shell $i = nl$, and is determined by the total potential φ from which the quantum-electron potential V_i^e is subtracted to prevent self-action. Exchange effects are neglected in this case. The subscript i in (4) runs through all the quantum shells nl, but matters are simplified by the fact that the equation for the ith ψ function does not contain the jth ψ function at $i \neq j$, i.e., these equations can be solved independently, and the interaction between the different electrons is taken into account via the total potential φ.

Note that a more correct allowance for the electron's own potential V_i^e in the Schrödinger equation (4) (compared with Refs. 7 and 8) ensures a Coulomb asymptotic behavior of the potential $U(r) = -1/r$ as $r \to \infty$, since $\varphi(r) \to 0$ and the quantum-electron potential has the Coulomb asymptote, i.e., $V_i^e = -1/r$. The ensuing transformation of (4) into an integro-differential equation does not complicate the calculations significantly, since introduction of the potential V_i^e perturbs the solution little (if $Z \gg 1$), and successive approximations yield rapid convergence after two or three iterations.

The set of equations (3) and (4) is self-consistent if it is assumed that in the given potential φ the phase space of all the quantum electrons and vacancies in the energy range from $-\infty$ to E_0 is exactly equal to

$$\Omega_0 = N_0 (2\pi)^3, \quad N_0 = \sum_{n=1}^{n_0} 2n^2,$$

where N_0 is the total number of electrons and vacancies for the quantum shells $n = 1$ to n_0, where n_0 is the maximum value of the principal quantum number of quantum electrons (thus, for $n_0 = 2$ we have $N_0 = 10$, $\Omega_0 = 80\pi^3$). This condition leads to an integral equation for the end-point energy E_0:

$$N_0 = \frac{2}{(2\pi)^3} \int_{-\infty}^{E_0} d\mathbf{p} \, d\mathbf{r} = \frac{2^{5/2}}{\pi} \int_0^{r_0} r^2 \, dr \int_{-\varphi}^{E_0} (E + \varphi)^{1/2} dE$$
$$= \frac{2^{7/2}}{3\pi} \int_0^{r_0(E_0)} r^2 \, dr (\varphi + E_0)^{3/2}, \quad E_0 = -\varphi(r_0). \tag{5}$$

As a check on (5), we show, for example, that it yields the correct values of the energy for an excited hydrogen atom ($E = -1/2n_0^2$) for a number N_0 of vacancies up to a specified level n_0, i.e.,

$$N_0 = \sum_{n=1}^{n_0} 2n^2 = \int 2n^2 \, dn \sim \frac{2}{3} n_0^3$$

(at $n \gg 1$). Substituting in (5) for $\varphi = 1/r$ a Coulomb potential in which the excited electron moves, we get

$$N_0 = \frac{2^{7/2}}{3\pi} \int_0^{1/|E_0|} r^2 \, dr \left(\frac{1}{r} - |E_0| \right)^{3/2} = \frac{2^{7/2}}{3\pi} |E_0|^{-3/2}$$
$$\times \int_0^1 t^{1/2} (1 - t)^{3/2} dt = \frac{2^{7/2}}{3\pi |E_0|^{3/2}} B\left(\frac{3}{2}, \frac{5}{2} \right) = \frac{1}{3 \cdot 2^{1/2}} |E_0|^{-3/2}, \tag{6}$$

i.e., $|E_0| = (3 \cdot 2^{1/2} N_0)^{-2/3}$. Substituting the value $N_0 = 2n_0^3/3$, we obtain the asymptotic region $n \gg 1$ the correct energy values $|E_n| = 1/2n_0^2$.

We note next that the total potential of the atom will be regarded as spherically symmetric, and we use accordingly in (1) and (3) the quantum-electron densities averaged over the component of the orbital momentum m:

$$\bar{\rho}_q = \sum_{nl} \frac{\xi_{nl}}{2l+1} \frac{R_{nl}^2(r)}{r^2} \sum_{m=-l}^{l} |Y_{lm}(\theta, \varphi)|^2$$
$$= \frac{1}{4\pi r^2} \sum_{nl} \xi_{nl} R_{nl}^2(r). \tag{7}$$

The average potential of the quantum electron is correspondingly

$$\bar{V}_{nl}^{e}=-\frac{1}{2l+1}\sum_{m=-l}^{l}\int\frac{|\psi_{nlm}|^{2}}{|\mathbf{r}-\mathbf{r}'|}d\mathbf{r}'$$

$$=-\frac{1}{r}+\int_{r}^{\infty}\left(\frac{1}{r}-\frac{1}{r'}\right)R_{nl}^{2}\,dr',\tag{8}$$

where $R_{nl}(r)$ are the radial wave functions of the quantum electron, normalized by the condition

$$\int_{0}^{\infty}R_{nl}^{2}\,dr=1.$$

We rewrite thus finally the set (3)–(5) in the form

$$\chi''=\frac{2^{7/2}}{3\pi}\frac{r}{Z}\left[\left(\frac{Z\chi}{r}\right)^{3/2}\theta(\chi)-\left(\frac{Z\chi}{r}+E_{0}-E_{F}\right)^{3/2}\theta(\varphi+E_{0})\right]+\frac{1}{Zr}\sum_{nl}\xi_{nl}R_{ln}^{2},\tag{9a}$$

$$R_{nl}''+2[E_{nl}+\varphi-V_{nl}^{e}-l(l+1)/2r^{2}]R_{nl}=0,\tag{9b}$$

$$N_{0}=\frac{2^{7/2}}{3\pi}\int_{0}^{r_{0}}r^{2}\,dr\left(\frac{Z\chi}{r}+E_{0}-E_{F}\right)^{3/2}.\tag{9c}$$

It must be emphasized that the presence of vacancies in the energy region $E<E_0$ is described in the set (9) semiclassically, as against the quantum treatment of the density at $E<E_0$. In another possible method, the decrease of the electron density on account of the vacancies is treated by quantum theory, and all the electrons of the atom are considered in a statistical model. This yields a self-consistent set of equations similar to (9) but simpler. In the quantum description of the vacancies (which can occupy arbitrary $i=nl$ shells, $i=1,\ldots,k$), the electron density is given by

$$\rho_{\Sigma}=2\sum_{nlm}|\psi_{nlm}|^{2}-\sum_{i=1}^{k}p_{i}|\psi_{nlm}|^{2},\tag{10}$$

where $p_i=2(2l+1)-\xi_{nl}$ is the number of vacancies in the $i=nl$ shell. The summation over nlm in (10) is over all the atom shells. In the semiclassical approximation, replacing the sums over n and l in (10) by integrals and averaging over the oscillations of the semiclassical radial functions, we obtain the usual TF-approximation expression (see Ref. 15 for details):

$$2\sum_{nlm}|\psi_{nlm}|^{2}=\frac{2}{4\pi r^{2}}\int R_{nl}^{2}(2l+1)\,dn\,dl$$

$$=\frac{2^{3/2}}{3\pi^{2}}(\varphi+E_{F})^{3/2}\theta(\varphi+E_{F}).\tag{11}$$

The charge-equilibrium equation takes in this case the form

$$\Delta\varphi=4\pi\rho_{\Sigma}=\frac{2^{7/2}}{3\pi}(\varphi+E_{F})^{3/2}\theta(\varphi+E_{F})-\sum_{nl}p_{nl}\frac{R_{nl}^{2}}{r^{2}}.\tag{12}$$

The averaging in (12) is over the magnetic numbers m of the vacancies, and the summation is over all nl shells in which vacancies are present. Introducing the screening function χ and adding the Schrödinger equations to Eq. (12) we obtain for the radial quantum functions R_{nl} the set of equations

$$\chi''=\frac{2^{7/2}}{3\pi}\left(\frac{Z}{r}\right)^{1/2}\chi^{3/2}\theta(\chi)-\sum_{nl}\frac{p_{nl}R_{nl}^{2}}{Zr},\tag{13a}$$

$$R_{nl}''+2[E_{nl}+\varphi-V_{nl}^{e}-l(l+1)/2r^{2}]R_{nl}=0.\tag{13b}$$

This set is particularly simple in the most prevalent case when vacancies are present in one n_0l_0 shell, for in this case Eq. (13a) need be solved simultaneously with only one Schrödinger equation for the n_0l_0 shell. The energies E_{nl} of the remaining shells can subsequently be found from Eq. (13b) with an already specified self-consistent potential φ. In the quantum treatment of the vacancies no difficulties are encountered in determining the end-point energy E_0, since all the electrons are described in the statistical model and occupy the energy spectrum from $-\infty$ to E_F, i.e., $E_0=-\infty$. Note that Eq. (13a) reduces the multivacancy-atom problem to the TF problem for an atom without vacancies, but with allowance for a certain external potential V_v that results from the vacancies and satisfies the relation

$$\Delta V_{v}=-\sum_{nl}p_{nl}\frac{R_{nl}^{2}}{r^{2}}.$$

In other words, the presence of vacancies can be taken into account by introducing into the TF equation an equivalent positive-charge distribution

$$\rho_{v}=\frac{1}{4\pi r^{2}}\sum_{nl}p_{nl}R_{nl}^{2}.$$

The description of the multivacancy atom with the aid of the system (13) turns out to be simpler, but has also some shortcomings compared with the system (9). It is easy to show that Eq. (13) just as in the usual TF model, leads to divergence of the electron density $\rho_\Sigma(r)\propto r^{-3/2}$ as $r\to 0$. It is known that this can lead to some errors in the determination of the total energy and of the electronic terms. One can easily find, for the system (9) with a restricted statistical-electron spectrum ($E_0<E<E_F$), that $\rho_\Sigma\propto r^{-1/2}$ as $r\to 0$ [see (2)], and that the errors due to this divergence become practically inessential (for details see Ref. 16 and also the results in Sec. 3).

Equations (9a) and (13a) should be solved subject to the usual boundary conditions

$$\begin{gathered}\chi(0)=1,\quad\text{i.e.,}\quad\varphi(r)=Z/r\quad\text{for}\quad r\to 0,\\ \chi(\infty)=0\quad\text{for}\quad E_{F}=0,\\ \chi'(r_{F})=E_{F}/Z,\quad\chi(r_{F})=0\quad\text{for}\quad E_{F}<0,\end{gathered}\tag{14}$$

where $r=r_F$ is the ion radius. The total number of the electrons is $N=N_e+N_q$, where N_q is the number of quantum electrons and N_e the number of statistical electrons:

$$N_{q}=\sum_{nl}\xi_{nl},\qquad N_{e}=\int_{0}^{r_{F}}4\pi\rho_{e}(r)r^{2}\,dr,$$

is easily determined by integrating Eq. (1) over the ion volume:

$$Z\int_{0}^{r_{F}}r\chi''\,dr=Z[r\chi'-\chi]\big|_{0}^{r_{F}}=E_{F}r_{F}+Z=N,\qquad Z_{F}=-E_{F}r_{F}=Z-N,\tag{15}$$

where Z_F is the total charge of the ion of given energy E_F. Since in the considered case of quantum electrons their orbits are smaller than the ion radius r_F, the boundary conditions for the Schrödinger equations (9b) and (13b) can be specified in the form $R_{nl}(0) = 0$, $R_{nl}(r_F) = 0$.

The system (9) or (13), with allowance for the boundary conditions, can be solved by an iteration method. A convenient zeroth approximation can be hydrogenlike functions with energies E_i determined by perturbation theory (see Appendix A). The total potential φ obtained by solving (9a) is used further to calculate new functions R_{nl}, values $N_0(E_0)$, and energies E_{nl} and E_0. The potentials V_i^e are determined by using the wave functions calculated in the preceding step. By varying E_0 and E_{nl} in the required directions with the aid of usual iteration methods (such as Newton's) we solve (9a) again, and so on. Three iterations usually suffice for convergence to obtain energy values that differ little from those of the preceding iteration.

In the case of an ion without vacancies, when all electrons are described by the TF mehtod, the following relations hold for the total atom energy $E = T$, see Refs. 7 and 17 (T is the electron kinetic energy and U the potential energy):

$$T={}^3/_5Z^2(\mu-J), \qquad U=-Z^2(\mu-J/2)+{}^1/_2E_F{}^2r_F, \tag{16}$$

where

$$\mu=-\chi'(0), \qquad J=\int_0^{r_F}\chi'^2\,dr, \qquad N_e=Z-Z_F=Z-r_F|E_F|.$$

Similar relations can be obtained also when the quantum and statistical electrons are segregated, i.e., for the system (9) (see Appendix B for the derivation):

$$\begin{gathered}T=\frac{3}{5}Z^2(\mu-J)-\frac{3}{5}|E_F|N_v+\frac{3}{5}|E_0|N_0\\+\frac{2}{5}\sum_{nl}\xi_{nl}\int_0^{r_F}R_{nl}{}^2\varphi\,dr-\sum_{nl}\xi_{nl}|E_{nl}|,\\U=-Z^2\left(\mu-\frac{J}{2}\right)+\frac{1}{2}E_F{}^2r_F-\sum_{nl}\xi_{nl}\int_0^{r_F}dr'R_{nl}{}^2\int_{r'}^{\infty}\frac{R_{nl}{}^2}{r''}dr''.\end{gathered}\tag{17}$$

It is seen that at $\xi_{nl} = 0$ Eqs. (16) and (17) are identical. Equations (17) permit calculation of the total energy of a multivacancy atom. In the quantum treatment of the vacancies [system (13)] the expressions for the potential and kinetic energies agree with Eqs. (16) (see Appendix B), i.e., the presence of vacancies changes the energy because the values of μ, J, and r_F are changed. In view of the virial theorem $2T = |U|$, we can exclude J and write the total energy $E = T + U$ in the form

$$E=T+U=-{}^3/_7\mu Z^2+{}^1/_2Z^2+{}^3/_7E_F{}^2r_F. \tag{18}$$

Note that the second term $Z^2/2$ is the Schwinger quantum correction[18] that eliminates the total-atom-energy overestimate due to the divergence of the statistical-electron density as $r\to 0$. This correction can be used also in the description of a multivacancy atom, inasmuch as in the model (13) the statistical electrons also occupy the entire spectrum $(-\infty, E_F)$.

3. CALCULATION RESULTS AND DISCUSSION

We analyze, by way of example, first the solution of the system (9) in the simplest case of two quantum $1s^2$ electrons and a statistical description of the electrons of shells $n\geqslant 2$. Figure 1a shows the calculated energy of the 1s shell for the case $Z = 29$ (copper) vs the value of E_0, i.e., vs the phase volume $\Omega_0 = (8\pi)^3N_0$ contained in the TF potential φ in the energy interval $(-\infty, E_0)$. The values of E_0 shown in Fig. 1a were determined by iteration from Eq. (9a). It can be seen that the calculated E_{1s} agrees with good accuracy (0.2%)[1)] with the experimental 1s-shell energy (dashed in Fig. 1a: $E_{1s} = 329$ a.u.) precisely at $N_0(E_0) = 2$. This is as expected, for in this case the phase volume $\Omega_0 = 16\pi^3$ not filled with statistical electrons is occupied by two quantum $1s^2$ electrons, and the system (9) describes in a self-consistent manner the vacancy-free atom. It can also be seen that neglect of the phase volume occupied by the quantum electrons [this corresponds to $N_0(E_0) = 0$ and $E_0\to -\infty$] leads to substantially lower 1s-shell energy, $E_{1s} = 300$ a.u. The 1s-level energy is most sensitive to the value of E_0 (see Fig. 1), therefore the use of Eq. (9c) to determine the lower limit E_0 of the spectrum of the statistical electrons is essential for the self-consistency of the system (9) and for a best fit to the experimental data.

Note that the calculated values of the energy of the 1s electrons obtained at values $N_0 > 2$, for example at $N_0 = 4$ and 10, shows that the binding energy E_{1s} increases when vacancies appear in the $n = 2$ shell (two and eight vacancies, respectively). The energy $E_{1s} = 358$ a.u. at $N_0 = 10$ corresponds here to the binding energy of the 1s shell when the $n = 2$ shell is entirely empty, while the energy $E_0 = 19.7$ a.u. at $N_0 = 10$ shows the lower limit for statistical electrons of the $n = 3$ shell. Accordingly, at $N_0 = 2$ the value $E_0 = 109$ a.u. corresponds approximately to the lower limit of the TF electrons of the $n = 2$ shell. Note that the experimental values of the quantum energies of the shells $L_{\rm I}$ and $L_{\rm II,III}$ (40 and 35 a.u., respectively) turn out to be much higher than

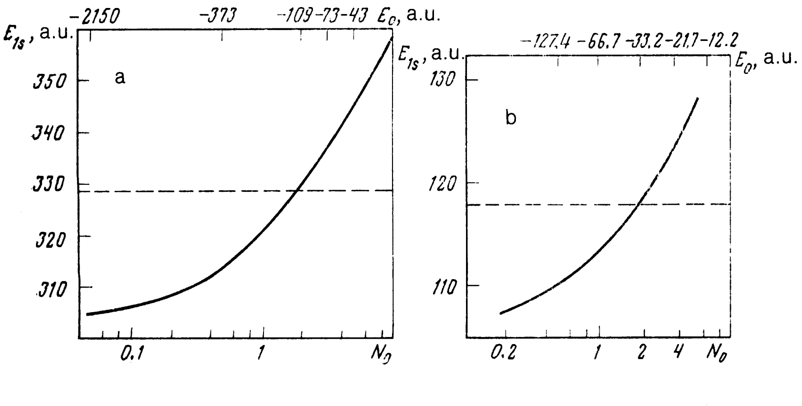

FIG. 1. Dependence of the 1s shell energy for copper atoms (a), $Z = 29$, and for argon atoms (b), $Z = 18$, on the number N_0 of states contained in the potential φ below the energy limit E_0 of the statistical electrons. Dashed—experimental 1s-state energies.

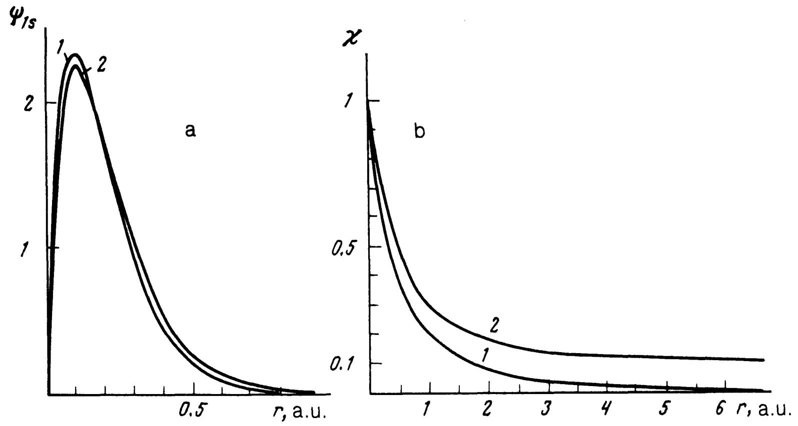

FIG. 2. (a) Wave functions of $2s$ states of the hydrogenlike ion Ne^{9+} (curve 1) and of the Ne atom (curve 2). b) Screening functions $\chi = r\varphi/Z$ (curve 1) and $\chi_1 = rU(r)/Z$ (curve 2) for the potential $U(r)$ in the Schrödinger equation of the $1s$ state of the Ne atom ($Z = 10$).

the boundaries of the spectra of the same shells when considered in the statistical model.

Analogous results are shown for $Z = 18$ (Ar) in Fig. 1b. Here, too, the best agreement between calculated energy of the $1s$ shell with the experimental value $E_{1s} = 118.5$ a.u. is observed for a phase volume $\Omega_0 = 16\pi r^3$, i.e., at $N_0 = 2$. Note that the energy $E_{1s} = 127$ a.u. obtained in the present calculation for $N_0 = 5$, i.e., for three vacancies in the $n = 2$ shell, is approximate, for in this case a uniform vacancy-density distribution is assumed in the phase space $d\mathbf{p}d\mathbf{r}$ in a certain energy interval, i.e., averaged over the orbital momenta. More accurate calculations, in which the vacancies are assumed to be concentrated in the $2p$ shell, are presented below in the quantum description of electrons at $n = 2$.

By way of example, Figure 2a shows the variation of the $1s$-state wave function for the hydrogenlike ion Ne^{9+} (curve 1) and for neutral neon $Ne(1s^2 2s^2 2p^6)$ (curve 2), obtained by statistical treatment of electrons with $n = 2$ (i.e., $N_0 = 2$). Figure 2b shows the values, obtained in the same calculation, of the screening function (curve 1) for the total potential $\chi = r\varphi/Z$, and also the function $\chi_{1s} = rU(r)/Z$ (curve 2) that characterizes the potential for a quantum electron of the $1s$ shell. The asymptotic value $\chi_{1s}(\infty) = 0.1$ (see Fig. 2b) leads to a Coulomb asymptotic relation for the potential $U(r) = Z\chi_{1s}(\infty)/r \approx 1/r$ at $Z = 10$. The calculations presented show also that introduction of a vacancy in the $2s$ shell of $Ne(1s2s^2 2p^6)$ increases considerably the $1s$-electron binding energy, by $\Delta E_{1s} = 106.9$ eV, in view of the decrease of the screening of the nuclear field, while the relative charge of the $1s$ electron energy [i.e., the quantity $2\Delta E_{1s}/Z^2$, $\Delta E = E_{1s}(1s^2...) - E_{1s}(1s...) > 0$] decreases with increase of the charge Z, since the effective potential $U(r)$ for the $1s$ electron approaches the Coulomb potential (Z/r) at distances of the order of the orbit size. The corresponding calculations with allowance for vacancies in the $1s$ shell were made for $Z = 10$, 18, 29, and 42 (a statistical trial was used for $n \geqslant 2$ electrons) and yielded the following approximation of the dependence of $2\Delta E_{1s}/Z^2$ on the nuclear charge Z:

$$(2\Delta E/Z^2)\,[\text{a.u.}] = 0.446 Z^{-1/3} - 0.015, \qquad 10 \leqslant Z \leqslant 60.$$

Figure 3 shows comparisons of the following: a) the total energies of the atoms Ne, Ar and Cu calculated from Eqs. (17) with quantum description of $1s^2$ electrons, b) the results of the usual TF model [i.e., Eqs. (16)], c) Hartree-Fock calculations.[20] It can be seen that the quantum description of the $1s^2$ electrons makes it possible to obtain a substantially more accurate agreement with the Hartree-Fock data. As already discussed above, this is due to the more correct behavior of the density of the statistical electrons in the region of the nucleus when lower limits are imposed on the spectra of these electrons (i.e., $E > E_0$). Note that, for the same reason, calculation of the $1s$-state energy in the Ar atom turns out to be more accurate ($\approx 0.4\%$) upon a semiclassical introduction of the vacancies, i.e., when the system (9) is used. However, calculations using the simpler system (13) also provide a sufficiently accurate (≈ 1–2%) description of the shell energies. For more complicated situations, when the vacancies are concentrated in shells $n > 1$, it is therefore more convenient to use Eqs. (13) for the calculations. We have used these equations in calculation for multivacancy atoms $Ar(1s^2 2s^2 2p^m 3s^2 3p^6)$ with vacancies $v = 6 - m$, concentrated in the $2p$ shell. Together with the statistical TF equation (13a) we solved here only one quantum equation for the $2p$ shell, and the energies of the $2s$ and $3p$ states were calculated with the aid of (13b) already after the self-consistent potential φ was determined.

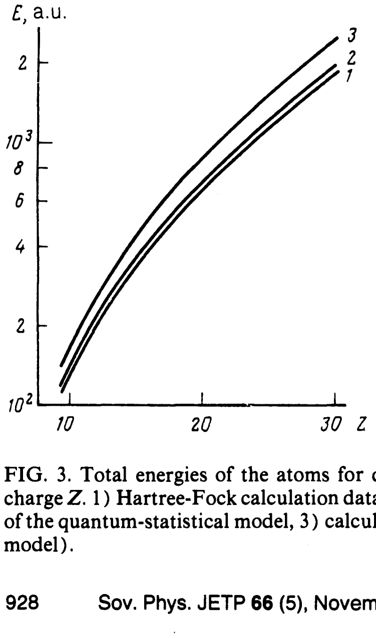

FIG. 3. Total energies of the atoms for different values of the nuclear charge Z. 1) Hartree-Fock calculation data,[20] 2) calculated with Eqs. (7) of the quantum-statistical model, 3) calculation with Eqs. (16) of the TF model).

In the absence of vacancies, the calculations yield for the transitions $K_\alpha\,(2p \to 1s)$ and $K_\beta\,(3p \to 1s)$ the respective energies 3007 and 3230 eV, in satisfactory agreement with the experimental data (2957.01 and 3190.5 eV). Calculation shows that the energies of the K_α and K_β radiation increase approximately linearly with increase of the number of vacancies in the $2p$ shell ($v = 0$–5), while the energy increments ΔE_{K_α} and ΔE_{K_β} of the corresponding lines can be approximated by the formulas

$$\Delta E_{K_\alpha} \approx 18v \ [\text{eV}], \quad \Delta E_{K_\beta} = 42v \ [\text{eV}].$$

It is seen that the appearance of multiple vacancies in the $n = 2$ shell shifts the energies of the K_α and k_β transitions by amounts ΔE on the order of 100–200 eV. This agrees well with the opinion that the experimentally obtained[2] shifts and widths of the K_α and K_β lines are due to the presence of several vacancies in the $n = 2$ shell and to a random scatter of their number for different Ar^{17+} ions recombining on the solid surface. The results for the shifts of the K_α and K_β lines in the multivacancy atom Ar ($Z = 18$) agree with detailed Hartree-Fock calculations[6] (the calculation accuracy decreases somewhat with increase of v, so that the deviation from Ref. 6 does not exceed 2–3% for the K_α line and 5–10% for K_β).

Note that application of the calculations performed here in the framework of a quantum-statistical model to the case of larger values of Z entails no significant complications, since it does not add to the total number of equations, and only changes the parameters. For the Hartree-Fock method, however, the calculations at higher values of Z leads to a substantial increase of the computational difficulties. Therefore the use of the model proposed here can be useful for the description of x-ray or Auger spectra of multivacancy atoms.

APPENDIX A

The energies of the internal, $1s$, $2p$, and $2s$ electrons in the absence of vacancies in an atom ($Z \gg 1$) can be estimated by perturbation theory. We choose as the zeroth approximation Coulomb wave functions in an unscreened field of the nucleus, and as the perturbation the difference between the TF and Coulomb potentials, i.e., $V(r) = Z(1 - \chi)/r$; for the screening function we use the Teitz approximation[17]

$$\tilde{\chi}(x) = (1+\alpha x)^{-2}, \tag{A1}$$

where

$$x = rZ^{1/3}/b, \quad b = 0.885, \quad \alpha = 0.53625.$$

The shift of term nl can be calculated by perturbation theory with the aid of the equation

$$\Delta E_{nl} = Z\int_0^\infty R_{nl}^2\left[1-\tilde{\chi}\left(\frac{r}{b}Z^{1/3}\right)\right]dr. \tag{A2}$$

Substituting in (A2) the unperturbed hydrogenlike wave functions of the $1s$, $2s$, and $2p$ states for an ion of charge Z (see, e.g., Ref. 21) and calculating the corresponding integrals, we get

$$\begin{aligned}
\Delta E_{1s} &= Z^2[1+\beta_1^2-\beta_1^2 e^{\beta_1}E_1(\beta_1)(1+\beta_1)],\\
\Delta E_{2s} &= {}^1/_8 Z^2[\beta_2^2+6\beta_2^3+7\beta_2^2+2-\beta_2^2E_1(\beta_2)\\
&\quad \times e^{\beta_2}(\beta_2^3+7\beta_2^2+12\beta_2+4)],\\
\Delta E_{2p} &= \frac{1}{24}Z^2[\beta_2^4+2\beta_2^3-\beta_2^2+6-\beta_2^4(3+\beta_2)e^{\beta_2}E_1(\beta_2)],
\end{aligned} \tag{A3}$$

where

$$\beta_1 = \frac{2b}{\alpha}Z^{1/3}, \quad \beta_2 = \frac{\beta_1}{2}, \quad E_1(x) = \int_x^\infty \frac{e^{-t}}{t}dt.$$

Since the use of perturbation theory is justified only for large Z and accordingly $\beta \sim Z^{2/3} \gg 1$, it is convenient to use asymptotic expansions of Eqs. (A3) in reciprocal powers $\beta \sim Z^{2/3}$. The corresponding algebra yields

$$\begin{aligned}
\Delta E_{1s} &= 1.21Z^{4/3}[1-1.36Z^{-2/3}+2.2Z^{-4/3}-4.17Z^{-2}+\ldots],\\
\Delta E_{2s} &= 1.21Z^{4/3}[1-5.45Z^{-2/3}+30.85Z^{-4/3}-184Z^{-2}+\ldots],\\
\Delta E_{2p} &= 1.21Z^{4/3}[1-4{,}55Z^{-2/3}+22Z^{-4/3}-117Z^{-2}+\ldots],
\end{aligned} \tag{A4}$$

where the expansions (A4) that include terms $\sim Z^{-2}$ can be used for $1s$ states at $Z > 5$–7, and for $2s$ and $2p$ levels at $Z > 35$–40. Note that a perturbation-theory calculation for the $1s$ states was carried out earlier in Ref. 17. The calculations presented here for $2s$ and $2p$ states can also be useful for estimates of shell energies in the zeroth approximation of the considered iteration problem (9) or (13), and also to deduce the analytic dependences of the transition energies on the nuclear charge Z.

APPENDIX B

We calculate the total energy of a multivacancy atom. It is convenient to rewrite the expression for the kinetic energy of the statistical electrons in the form

$$\begin{aligned}
T_e &= \frac{2}{(2\pi)^3}\int\frac{p^2}{2}d\mathbf{p}\,d\mathbf{r} = \frac{2^{7/2}}{5\pi}\int_0^{r_F} r^2\,dr[(\varphi+E_F)^{5/2}-(\varphi+E_0)^{5/2})]\\
&= \frac{3}{5}\int_0^{r_F}\varphi\rho_e\,dr + \frac{3}{5}E_F(N_0+N_e) - \frac{3}{5}N_0E_0.
\end{aligned} \tag{B1}$$

Taking into account the following relations

$$\Delta\varphi_e = 4\pi\rho_e, \quad \Delta V_q = 4\pi\rho_q,$$

$$\varphi = \varphi_e + V_q + \frac{Z}{r}, \quad \rho_q = \sum_{nl}\frac{\xi_{nl}}{4\pi r^2}R_{nl}^2,$$

$$rV_q = \sum_{nl}\xi_{nl}\left[-1+\int_r^{r_F}\left(1-\frac{r}{r'}\right)R_{nl}^2\,dr'\right],$$

$$(rV_q)_r' = -\sum_{nl}\xi_{nl}\int_r^{r_F}\frac{R_{nl}^2}{r'}dr',$$

we calculate the integral in (B1)

$$\int\varphi\rho_e\,d\mathbf{r} = \int_0^{r_F} r\varphi(r\varphi_e)''\,dr = \int_0^{r_F} r\varphi(r\varphi)''\,dr - \int_0^{r_F} r\varphi(rV_q)''\,dr.$$

Integrating by parts and using the boundary conditions (14), we get

$$\begin{aligned}
\int_0^{r_F} r\varphi(r\varphi)''\,dr &= r\varphi(r\varphi')\Big|_0^{r_F} - \int_0^{r_F}(Z\chi'-E_F)^2\,dr\\
&= Z^2(\mu-J) - E_F(Z+E_Fr_F),
\end{aligned} \tag{B2}$$

$$\begin{aligned}
\int_0^{r_F} r\varphi(rV_q)''\,dr &= r\varphi(rV_q)'\Big|_0^{r_F} + \int_0^{r_F}(r\varphi)'\,dr\sum_{nl}\xi_{nl}\int_r^{r_F}\frac{R_{nl}^2}{r'}dr'\\
&= \sum_{nl}\xi_{nl}\int_0^{r_F}R_{nl}^2\varphi\,dr,
\end{aligned}$$

where

$$\mu=-\chi'(0),\qquad J=\int_0^{r_F}\chi'^2\,dr.$$

We obtain the kinetic energy of the quantum electrons by using the quasiclassical approximation:

$$T_q=\int^{r_F}\frac{p^2}{2}R_{nl}{}^2\,dr=-\sum_{nl}\xi_{nl}|E_{nl}|+\sum_{nl}\xi_{nl}\int_0^{r_F}\varphi R_{nl}{}^2\,dr. \quad \text{(B3)}$$

For the total kinetic energy we obtain ultimately

$$T=T_e+T_q=\frac{3}{5}Z^2(\mu-J)+\frac{3}{5}N_vE_F-\frac{3}{5}N_0E_0$$
$$+\frac{2}{5}Z\sum_{nl}\xi_{nl}\int_0^{r_F}\frac{R_{nl}{}^2}{r}\chi\,dr-\sum_{nl}\xi_{nl}|E_{nl}|, \quad \text{(B4)}$$

where $N_v=N_0-N_q$ is the number of vacancies.

The potential energy of the statistical electrons is determined by their interaction with the nucleus, with the quantum electrons, and with one another:

$$U_e=-\frac{1}{2}\int\rho_e\varphi_e\,d\mathbf{r}-Z\int\frac{\rho_e}{r}\,d\mathbf{r}-\int V_q\rho_e\,d\mathbf{r}$$
$$=-\frac{1}{2}\int\rho_e\varphi\,d\mathbf{r}-\frac{Z}{2}\int\frac{\rho_e}{2}\,d\mathbf{r}-\frac{1}{2}\int V_q\rho_e\,d\mathbf{r}. \quad \text{(B5)}$$

For the potential energy of the quantum electrons, we take into account the interaction with the nucleus and with one another, subtracting the "self-action" of the quantum electrons:

$$U_q=-Z\int\frac{\rho_q}{r}\,d\mathbf{r}-\frac{1}{2}\int V_q\rho_q\,d\mathbf{r}$$
$$-\frac{1}{2}\sum_{nl}\xi_{nl}\int d\mathbf{r}\,d\mathbf{r}'\,\frac{\psi_{nl}{}^2(\mathbf{r})\,\psi_{nl}{}^2(\mathbf{r}')}{|\mathbf{r}-\mathbf{r}'|}. \quad \text{(B6)}$$

We reduce the total potential energy, after some transformations, to the expression

$$U=U_e+U_q=-\frac{Z}{2}\int\frac{\rho_\Sigma}{r}\,d\mathbf{r}-\frac{1}{2}\int\rho_\Sigma\varphi\,d\mathbf{r}$$
$$-\sum_{nl}\xi_{nl}\int_0^{r_F}dr'\,R_{nl}{}^2\int_{r'}^{r_F}\frac{R_{nl}{}^2}{r''}\,dr''.$$

Using Eq. (B2) for the integral

$$\int\rho_\Sigma\varphi\,d\mathbf{r}=\int_0^{r_F}r\varphi(r\varphi)''\,dr$$

and calculating the integral

$$\int\frac{\rho_\Sigma}{r}\,d\mathbf{r}=\int_0^{r_F}(r\varphi)''\,dr=Z_\mu+E_F,$$

we obtain ultimately

$$U=-Z^2\left(\mu-\frac{J}{2}\right)+\frac{1}{2}E_F{}^2r_F-\sum_{nl}\xi_{nl}\int_0^{r_F}dr'\,R_{nl}{}^2$$
$$\times\int_{r'}^{r_F}\frac{R_{nl}{}^2}{r''}\,dr'' \quad \text{(B7)}$$

The total energy is calculated in similar fashion also for the system (13), when all the electrons are described in the statistical TF model and the vacancies lead to the appearance of an external potential V_v, with

$$\Delta V_v=-4\pi\rho_v=-\sum_{nl}p_{nl}\frac{R_{nl}{}^2}{r^2}.$$

For the kinetic energy we obtain in this case

$$T_e=\frac{3}{5}\int(\varphi+E_F)\rho_\Sigma(r)\,d\mathbf{r}=\frac{3}{5}E_FN+\int_0^{r_F}r\varphi(r\varphi)''\,dr$$
$$=\frac{3}{5}Z^2(\mu-J). \quad \text{(B8)}$$

Here $\rho_\Sigma=\rho_e-\rho_v$ and $N=N_e-N_v$. Calculation of the potential energy of a multivacancy atom also leads to an equation identical with those of the usual TF model [see (16)]. The presence of vacancies is taken into account here by changing the values of μ, J, and r_F, which depend on the behavior of the screening function χ.

The author thanks Yu. V. Martynenko, O. B. Firsov, and M. I. Chibisov for a discussion of the results.

---

[1] So good an agreement with the experimental data is due in this case to the fact that for the 1*s*-shell energy the principal role is played by the Coulomb interaction of the electrons with the charge of the nucleus. Therefore, for example, the energies calculated below for the K_α and K_β lines of argon turn out to be less accurate, since they require calculation of the energies of the 2*p* and 3*p* states, for which the electron-electron interaction is more significant. These results can be refined by introducing exchange and quantum corrections into the TF equation (see, e.g., Ref. 19).

[1] J. D. Garcia, R. J. Forther, and T. M. Kavanagh, Rev. Mod. Phys. **45**, 111 (1973).
[2] E. D. Donets, V. A. Trifonov, G. A. Tutin, *et al.*, JINR preprint R7-83-627, 1983.
[3] C. P. Bhalla, N. O. Folland, and M. A. Hein, Phys. Rev. **A2**, 649 (1973).
[4] F. P. Larkins, Phys. Rev. **B9**, 129 (1971).
[5] R. J. Forther, R. C. Der, T. M. Kavanagh, and J. D. Garcia, *ibid.*, p. 53 (1972).
[6] C. P. Bhalla, Phys. Rev. **A8**, 2877 (1973).
[7] P. Gambos, *Die Statistische Theorie des Atoms und ihre Anwendungen*, Springer, 1949.
[8] R. Latter, Phys. Rev. **99**, 510 (1955).
[9] Yu. N. Demkov and N. B. Berezina, Opt. Spektrosk. **34**, 841 (1973).
[10] Yu. N. Demkov and N. B. Berezina, Zh. Eksp. Teor. Fiz. **68**, 848 (1975) [Sov. Phys. JETP **41**, 421 (1975)].
[11] K. L. Stepanov, Opt. Spektr. **38**, 3 (1975).
[12] B. F. Rozsnyai, J. Quant. Spectrosc. Rad. Transfer **15**, 695 (1975).
[13] S. Skupsky, Phys. Rev. **A21**, 1316 (1979).
[14] E. P. Bashkin, Zh. Eksp. Teor. Fiz. **82**, 1868 (1982) [Sov. Phys. JETP **55**, 1076 (1982)].
[15] A. B. Migdal and V.P. Krainov, *Approximation Methods in Quantum Mechanics*, Benjamin, 1969.
[16] E. S. Fradkin, Zh. Eksp. Teor. Fiz. **36**, 1533 (1959) [Sov. Phys. JETP **9**, 1087 (1959)].
[17] S. Flugge, Practical Quantum Mechanics, Springer, 1971, Vol. 2.
[18] J. Schwinger, Phys. Rev. **A4**, 2353 (1981).
[19] D. A. Kirzhnits, Yu. S. Lozovik, and G. V. Shpatkovskaya, Usp. Fiz. Nauk **117**, 3 (1975) [Sov. Phys. Usp. **18**, 649 (1975)].
[20] E. Clementi and C. Roetti, Atom. Data and Nucl. Data Tables, Vol. 14, p. 177 (1974).
[21] L. D. Landau and E. M. Lifshitz, *Quantum Mechancis, Nonrelativistic Theory*, Pergamon, 1978.
[22] M. A. Blokhin, X-ray Physics [in Russian], Nauka, 1953.

Translated by J. G. Adashko