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Semiclassical energy levels and the corresponding potentials in nonhydrogenic ions

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A semiclassical expression is derived for the potential seen by an nl-shell electron in a nonhydrogenic ion. Corresponding energies E_{nl} are compared with experimental values and with results of self-consistent-field calculations.

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I. INTRODUCTION

This work is intended to contribute to the semiclassical modeling of complex ions, in particular in the context of plasma-physics calculations. Though energy levels and wave functions of ions with many electrons can be obtained with high accuracy from self-consistent-field calculations, the semiclassical description is still very important since it allows one to calculate these quantities much faster and is more flexible when one wants to include perturbing effects of the neighborhood, such as in dense plasma environments. The ultimate goal is to compute plasma equation-of-state data and radiation coefficients accurately and fast enough for on-line use in radiation-hydrodynamics calculations. The potential of the semiclassical theory for this ambitious goal is far from being fully developed.

The screened hydrogenic model (SHM), first introduced by Slater [1] and recently improved by More [2], allows for a rapid determination of energy levels in arbitrary ions; however, within the hydrogenic approximation, the energies are degenerate for major n shells. The model has been found very useful for calculating equations-of-state of hot dense matter and also for calculating radiation coefficients [2,3] when complemented by the semiclassical expression for the oscillator strengths between n shells. For heavier elements, the restriction to hydrogenlike spectra becomes rather inaccurate, and the model was extended by Perrot [4] to include l splitting of the major n shells. It was studied in the extended form for plasma opacity calculations by Rickert and Meyer-ter-Vehn [5]. The SHM avoids dealing with wave functions explicitly; however, this becomes a problem when transitions between nl orbits are concerned.

The present work also builds up on the SHM, but makes systematic use of semiclassical WKB wave functions in addition. In this way, an analytic expression for the potential seen by an electron in a particular nl orbit is constructed in Sec. II and is used to determine energies E_{nl} via the Bohr-Sommerfeld quantization condition. In Sec. III, these energies are compared with experimental energies and with other theoretical calculations for some selected cases. In a companion paper [6], the energies are used to compute dipole matrix elements, again making use of WKB wave functions with appropriate phase shifts determined within the Coulomb approximation.

II. POTENTIAL EXPERIENCED BY nl-SHELL ELECTRONS

Energies E_{nl} of single-electron states with principal quantum number n and orbital quantum number l can be obtained in semiclassical approximation from the Bohr-Sommerfeld quantization condition [7]

$$\int_a^b P_{nl}(r)dr=\pi(n-l-\tfrac{1}{2}) \tag{1}$$

with the turning points a and b determined by $P_{nl}(a)=P_{nl}(b)=0$ and the momentum

$$P_{nl}(r)=\left[2E_{nl}+2V(r)-\frac{(l+\frac{1}{2})^2}{r^2}\right]^{1/2} . \tag{2}$$

Atomic units are used. The goal in this paper is to derive an analytic expression for the potential $V(r)$ in Eq. (2) and then to solve Eq. (1) for E_{nl}. This is achieved by a process of successive approximation.

Let us consider an electron in a particular state n_0l_0 of an ion with charge Z_{ion} and ask for the potential $V_{n_0l_0}(r)$, which this electron experiences in the field of the ionic core made up by the nucleus with charge Z and the other $(Z-Z_{\text{ion}}-1)$ electrons. The corresponding electrostatic potential

$$V^{\text{el}}_{n_0l_0}(r)=\frac{Z}{r}-\frac{4\pi}{r}\int_0^r \rho^{n_0l_0}(r')r'^2dr' -4\pi\int_r^\infty \rho^{n_0l_0}(r')dr' \tag{3}$$

is obtained from the charge density

$$\rho^{n_0l_0}(r)=\sum_{n,l} N_{nl}^{n_0l_0}\rho_{nl}(r) , \tag{4}$$

where $N_{nl}^{n_0l_0}$ is the number of electrons in each nl shell, except for the shell n_0l_0, in which the electron in question is subtracted. The average density contribution $\rho_{nl}(r)=R_{nl}^2(r)/4\pi$ of each nl electron is constructed from the WKB radial wave functions [7]

$$R_{nl}(r)=\frac{A_{nl}}{rP_{nl}(r)^{1/2}}\cos\left[\int_a^r P_{nl}(r)dr-\frac{\pi}{4}\right] , \tag{5}$$

which again contain $P_{nl}(r)$ given by Eq. (2). The scheme of successive approximation, followed here, is to determine $P_{nl}(r)$ *at this point* on a more elementary basis, using the screened hydrogenic model (see, e.g., More [2] for details) as a zero-order estimate. It assumes that the energies

$$E_{nl}^{(0)}=E_n=+W_n-\frac{Q_n^2}{2n^2} \tag{6}$$

are hydrogenlike with

$$Q_n=Z-\sum_{m\,(\leq n)}\sigma(n,m)N_m\,,\quad W_n=\sum_{m\,(\geq n)}\frac{N_mQ_m}{m^2}\sigma(m,n)\,, \tag{7}$$

$N_n=\sum_l N_{nl}^{n_0l_0}$, and screening constants $\sigma(n,m)$; a good set of screening coefficients was given by More [2] and is used in the present work. The corresponding potential is $V^{(0)}(r)=-W_n+Q_n/r$. With these zero-order expressions $E_{nl}^{(0)}$ and $V^{(0)}(r)$, we obtain

$$P_{nl}^{(0)}=\left[-\frac{Q_n^2}{n^2}+\frac{2Q_n}{r}-\frac{(l+\frac{1}{2})^2}{r^2}\right]^{1/2} . \tag{8}$$

The normalization constants A_{nl} in Eq. (5) are obtained by setting $\cos^2(\cdots)=\frac{1}{2}$ in the normalization integral [7] and using the derivative of Eq. (1) with respect to n to determine the remaining integral; this leads to

$$A_{nl}^2\approx\frac{2}{\pi}\frac{\partial E_n}{\partial n}=\frac{2Q_n^2}{\pi n^3} . \tag{9}$$

Note that the terms $\partial W_n/\partial n$ and $(\partial Q_n^2/\partial n)/(2n^2)$ cancel each other. Averaging the shell densities $\rho_{nl}(r)$ by setting again $\cos^2(\cdots)=\frac{1}{2}$, one obtains

$$\rho_{nl}(r)\approx\langle R_{nl}(r)^2/(4\pi)\rangle=\frac{Q_n^2}{4\pi^2n^3r^2P_{nl}^0(r)} , \tag{10}$$

and, performing the integration in Eq. (3) after insertion of Eqs. (10) and (4), an analytic expression for the electrostatic potential is obtained in the form

$$V_{n_0l_0}^{\mathrm{el}}(r)=\frac{1}{r}\left[Z-\frac{1}{\pi}\sum_{n,l}\frac{N_{nl}^{n_0l_0}}{n^2}\Omega_{nl}(r)\right] , \tag{11}$$

with

$$\Omega_{nl}=\begin{cases}\pi n^2 \quad \text{for } \Theta_{nl}<-1\\ -nrP_{nl}^{(0)}(r)+(Q_nr-n^2)\arcsin\Theta_{nl}(r)\\ \qquad\qquad +\frac{\pi}{2}(Q_nr+n^2) \quad \text{for } |\Theta_{nl}|\leq 1\\ \pi Q_nr \quad \text{for } \Theta_{nl}>1\end{cases}$$

and

$$\Theta_{nl}(r)=\left[1-\frac{Q_nr}{n^2}\right]\Big/\left[1-\frac{(l+1/2)^2}{n^2}\right]^{1/2} .$$

The total potential, felt by an electron in the n_0l_0 orbit and used in Eqs. (1) and (2) to calculate its energy $E_{n_0l_0}$, is obtained by adding the exchange potential

$$V_{n_0l_0}(r)=V_{n_0l_0}^{\mathrm{el}}(r)+V_{n_0l_0}^{\mathrm{ex}}(r) , \tag{12}$$

taken here in the local-density form

$$V_{n_0l_0}^{\mathrm{ex}}(r)=\alpha\left[\frac{3}{\pi}\rho^{n_0l_0}(r)\right]^{1/3} . \tag{13}$$

TABLE I. Inner-shell energies of Ar^+ in Ry. Present results are compared with different versions of self-consistent-field calculations [9].

State	Hartree-Fock		HFS-X_α [8]	This calculation
1s	238.3	233.7	229.4	239.4
2s	25.7	24.0	22.6	24.4
2p	20.2	19.3	17.8	20.5
3s	3.42	3.06	2.58	3.91
3p	2.09	1.97	1.53	2.83

The results are not strongly dependent on the strength parameter α, and a good overall fit to the data discussed in the next section was obtained with $\alpha=0.5$. This is less than the value $\alpha=1$, which is commonly used [8], but one should note that one part of the exchange interaction just compensates for the self-interaction of the electrons and that this self-interaction is already explicitly excluded in the present model.

III. RESULTS AND COMPARISON

The potential of Eq. (12), inserted into Eq. (2), is now used to calculate energies E_{nl}, solving Eq. (1) by numerical integration and iteration; such a scheme is rapidly converging. In Tables I–IV, we give some sample energies and compare with values taken from the literature. In Table I, we compare present results with different versions of self-consistent-field calculations for inner-shell energies of Ar^+, taken from Ref. [9]; it is seen that the general agreement is good and, in particular, that the deviations of the present results from the Hartree-Fock (HF) results are not larger than the differences of the

TABLE II. Inner-shell energies of Au^{25+} including the relativistic correction of Eq. (14); the deviations are with respect to relativistic HFS calculations of Yabe and Goel [10].

State	Energy (eV)	Deviation (%)
$1s,j=\frac{1}{2}$	81 507	0.35
$2s,j=\frac{1}{2}$	14 863	1.75
$2p,j=\frac{1}{2}$	14 462	0.68
$3s,j=\frac{1}{2}$	4040.3	3.4
$3p,j=\frac{1}{2}$	3831.3	2.4
$3d,j=\frac{3}{2}$	3217.7	4.5
$4s,j=\frac{1}{2}$	1397.6	5.7
$4p,j=\frac{1}{2}$	1303.4	4.8
$4d,j=\frac{3}{2}$	1112.6	3.3
$4f,j=\frac{5}{2}$	889.1	8.7

TABLE III. Inner-shell energies of different iron ions; deviations are given with respect to HF calculations quoted in [11].

Ion	States	Energy (eV)	Deviation (%)
Fe^{9+}	1*s*	7356	0.2
	2*s*	1065	3.2
	2*p*	974	1.0
	3*s*	304	2.5
Fe^{6+}	1*s*	7258	0.04
	2*s*	960	3.0
	2*p*	866	1.0
	3*s*	219	1.8
	3*p*	188	4.4
Fe^{3+}	1*s*	7167	0.1
	2*s*	865	5.2
	2*p*	771	0.6
	3*s*	141	6.6
	3*p*	110	0.2

TABLE IV. Ionization energies of excited states in Ar atoms in Ry units; values of the present model are compared with experimental and HF values [11].

Configuration	Present model	Hartree-Fock	Experiment
$3p^5 6p$	0.0565	0.0538	0.0495
$3p^5 6s$	0.0705	0.0670	0.0631
$3p^5 5d$	0.0400	0.0440	0.0409

various self-consistent-field methods among themselves.

In Table II, inner-shell energies of the high-Z ion Au^{25+} are given, including relativistic corrections according to Sommerfeld's formula

$$\Delta E_{nlj} = \frac{1}{137}^2 [3/(4n) - 1/(j+\tfrac{1}{2})] Q_n^4/(2n^3) \; ; \tag{14}$$

deviations from relativistic Hartree-Fock-Slater (HFS) calculations [10] are generally below 5% except for the least bound level with 8.7%.

Results for different Fe ions are shown in Table III. Differences between the semiclassical results obtained in this paper and the HF results quoted in [11] are again below 5% and become smaller for higher ionization degrees. Even for highly excited states in neutral Ar, the accuracy of the present model is not worse than corresponding HF calculations when comparing with experimental results; this is shown in Table IV. It is concluded that the simple semiclassical description for *nl*-shell energies developed in this work agrees quite well with much more time consuming HF calculations, especially for highly ionized ions and tightly bound electrons.

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[1] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[2] R. M. More, J. Quant. Spectrosc. Radiat. Transfer **27**, 345 (1982).

[3] G. D. Tsakiris and K. Eidmann, J. Quant. Spectrosc. Radiat. Transfer **38**, 353 (1987).

[4] F. Perrot, Phys. Scr. **39**, 332 (1989).

[5] A. Rickert and J. Meyer-ter-Vehn, Laser Part. Beams **8**, 715 (1990).

[6] P. Pankratov and J. Meyer-ter-Vehn, following paper, A **46**, 5500 (1992).

[7] L. D. Landau and E. M. Lifshitz, *Quantum Mechanics* (Pergamon, Oxford, 1977).

[8] J. C. Slater, *The Calculation of Molecular Orbitals* (Wiley, New York, 1979).

[9] P. P. Szydlik and A. E. S. Green, Phys. Rev. A **9**, 1885 (1974).

[10] T. Yabe and B. Goel, Kernforschungzentrum Karlsruhe Report No. KfK-4176, Karlsruhe, 1986 (unpublished).

[11] F. J. Rogers, B. G. Wilson, and C. A. Iglesias, Phys. Rev. A **38**, 5007 (1988).