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FAST COMPUTATION OF ELECTRONIC STRUCTURE IN PLASMAS. THE SCREENED HYDROGENIC MODEL WITH L-SPLITTING

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Résumé - A partir d'un minimum de données qui sont le numéro atomique Z et l'ensemble des populations pour les différentes couches électroniques de nombre quantique principal n , le Modèle Hydrogène Ecrané, dans sa version traditionnelle, permet le calcul très rapide de l'énergie totale, des niveaux électroniques et des potentiels d'ionisation pour un ion libre quelconque. Le but du présent travail est d'étendre ce modèle en y levant la dégénérescence en moment angulaire électronique l . Ce but est atteint grâce à la prise en compte d'un nombre réduit de nouvelles constantes données analytiquement en fonction des nombres quantiques.

Abstract - Starting with a minimum of input data which are the atomic number Z and the populations in the various n -shells of electrons, the Screened Hydrogenic Model, in its standard version, allows the calculation of the total energy, one-electron levels and ionization potentials for any free-ion configuration. The aim of the present work is to extend the model by including electron angular momentum splitting. This is achieved by taking into account a limited set of new constants which are given in compact analytic form in terms of the quantum numbers.

1 - INTRODUCTION

The numerical simulation of plasmas in various physical time-dependent conditions becomes more and more common. Such simulations, especially in the case of high- Z ions, require a very large amount of electronic data. Thus, the problem arises to calculate "on-line", at the moment they are needed, quantities such as the ion total energy, the one-electron energy levels and the successive ionization potentials. The computation must be very fast because it has to be repeated many times and constitutes only a (very?) small fraction of the numerical work.

The Screened Hydrogenic Model (SHM) is an efficient and well-known solution to this problem /1/. Let us consider an ion having populations P_n in its electron shells, labelled by the principal quantum number n . As shown by More /1/ the total energy is given by

$$E = - \frac{1}{2} \sum_n P_n Q_n^2 n^{-2} \quad (1)$$

Q_n is an effective charge, different in each shell, which is to be calculated according to the follo-

wing formula

$$Q_n = Z - \sum_{m \leq n} \sigma_{nm} \left(1 - \frac{1}{2} \delta_{nm}\right) P_m \quad (2)$$

The σ_{nm} are the so-called screening constants, elements of a triangular 10×10 matrix (55 numbers). The screening constants proposed by More /1/ are of particular interest because they have been chosen in order to reproduce as well as possible the ionization potentials given by Hartree-Fock-Slater calculations relative to a large number of ions. The one-electron energies \mathcal{E}_n satisfy the consistency equation

$$\mathcal{E}_n = \frac{\partial E}{\partial P_n}$$

or, explicitly

$$\mathcal{E}_n = -\frac{1}{2} Q_n^2 n^{-2} + \sum_{m \neq n} P_m Q_m m^{-2} \sigma_{mn} \left(1 - \frac{1}{2} \delta_{mn}\right) \quad (3)$$

Eqs.(2,3) are derived in /1/ using the notions of inner and outer screening of the atom or ion nucleus by the bound electrons. It will be helpful for our purpose to recall, in the following Section, that they can be obtained in a more general way using a variational principle.

2 - INTERPRETATION OF THE SHM IN TERMS OF ONE-ELECTRON DENSITIES

Let us try to represent the wave-function of a bound electron in the subshell n, l by an hydrogenic wave-function depending on an effective charge Q_n . In principle, Q should depend on both quantum numbers but, for the sake of simplicity, we neglect the l -dependence which is often weak, at least in the most internal shells. It is a well-known property of hydrogenic wave-functions that the average value of the kinetic energy operator (i.e., $\frac{1}{2} Q^2 n^{-2}$) does not depend on the electron angular momentum. The same property holds for the average value of $\frac{1}{r}$ (i.e., $Q n^{-2}$) which determines the electron-nucleus interaction. Thus, the only part of the total Hamiltonian expectation value where l does enter is the electron-electron interaction (again, under the assumption of a same effective charge Q_n within a given shell).

The one-electron density associated with the hydrogenic wave-function is of the form

$$\rho_{nl} = Q_n^3 f_{nl}(Q_n r) \quad (4)$$

Now, if l -splitting is omitted, an average density $\bar{\rho}_n$ is used for any state within the n -shell. This density may be written

$$\bar{\rho}_n = \sum_1 p_{n1} \rho_{n1} \quad (5)$$

where the p_{n1} are weights, the sum of which equals 1. It can be easily shown /2/ that the electrostatic interaction between the two densities $\bar{\rho}_n$ and $\bar{\rho}_m$ may be written $Q_n n^{-2} i_{nm}$ if $m \leq n$. To establish this formula, use has been made of the symmetry properties of the Coulomb integral; furthermore, with some other minor approximation, i_{nm} can be considered as a pure number. For any particular choice of the weights p_{n1} in Eq.(5), one gets a different set of numbers i_{nm} . The screening constants

σ are nothing but a special set of i .

All the contributions to the Hamiltonian expectation value may now be gathered to give

$$\langle H \rangle = \sum_n P_n \left(\frac{1}{2} Q_n^2 - Z Q_n\right) n^{-2} + \sum_{m \leq n} P_m P_n Q_m n^{-2} \sigma_{nm} \left(1 - \frac{1}{2} \delta_{nm}\right) \quad (6)$$

The minimization of $\langle H \rangle$ with respect to any charge Q_n leads to Eq.(2). We don't discuss here the role of the orthogonality constraints between one-electron wave-functions with the same angular momentum but different principal quantum numbers, or between excited states and the ground state of the ion.

3 - INCLUDING L-SPLITTING IN THE SHM

In this Section we show how the effect of l-splitting can be described in a simple way which keeps the efficiency of the SHM. This is achieved by using first order perturbation theory. The perturbation is, in each sub-shell n, l , the change in density which results from using the true density ρ_{nl} instead of the average density $\bar{\rho}_n$ defined in Eq.(5). As we have seen in the previous Section neither the kinetic energy nor the electron-nucleus interaction depend on l ; thus, only the electron-electron interaction will give a perturbation in the Hamiltonian expectation value. This perturbation is

$$\langle \Delta H \rangle = \sum_m \sum_{nl} P_m P_{nl} (\rho_{nl} - \bar{\rho}_n) \cdot \bar{v}_m \quad (7)$$

where we have used the notation $f \cdot g$ for the integral of the product of functions f and g in the whole r -space. \bar{v}_m is the Coulomb potential created by the average density $\bar{\rho}_m$. The total population in the shell n is $P_n = \sum_l P_{nl}$. Now, the calculation of $\langle \Delta H \rangle$ is significantly simplified by the following approximation.¹ Let us expand the potential \bar{v}_m around the center r_n of the shell n where the densities ρ_{nl} and $\bar{\rho}_n$ have their maximum. One gets

$$\bar{v}_m(r) = \frac{1}{r} \int_0^{r_n} \bar{\rho}_m r^2 dr + \int_{r_n}^{\infty} \bar{\rho}_m r dr - \frac{1}{2} \frac{(r-r_n)^2}{r} r_m \bar{\rho}_m(r_n) + O((r-r_n)^3) \quad (8)$$

The first two terms in this expansion do not contribute to the integral in Eq.(7) because they are an average of $\frac{1}{r}$ (identical for any hydrogenic state in shell n) and a constant. The last term only does contribute, so that

$$\begin{aligned} \langle \Delta H \rangle &= - \sum_m \sum_{nl} P_m P_{nl} q_{mn} Q_n^{-2} g_{nl} \quad (9) \\ q_{mn} &= \frac{1}{2} \bar{\rho}_m(r_n) r_n^3 \\ g_{nl} &= (\rho_{nl} - \bar{\rho}_n) \cdot (r r_n^{-1} - 2 + r_n r^{-1}) \end{aligned}$$

Now, one can proceed to the minimization of the modified form $\langle H + \Delta H \rangle$ of the Hamiltonian expectation value. This yields the new expression of the effective charges

$$\begin{aligned} Q_n &= Z - \sum_{m \leq n} \sigma_{nm} (1 - \frac{1}{2} \delta_{nm}) P_m + \sum_m P_m q_{mn} S_n \quad (10) \\ S_n &= \sum_{l=0}^{n-1} P_{nl} P_n^{-1} g_{nl} \end{aligned}$$

The additional constants required to describe l-splitting have very simple analytic forms. The WKB method has been applied to the calculation of q_{mn}

$$q_{mn} = \frac{1}{\pi} \left(\frac{n}{m} \right)^5 \left[2 - \left(\frac{n}{m} \right)^2 \right]^{1/2} \quad (11)$$

if $2m^2 \geq n^2$ and $q_{mn} = 0$ otherwise. For g_{nl} , one finds easily the exact result

$$g_{nl} = \frac{1}{4} n^{-2} \left[n^2 - 2l(1+l) - 1 \right] + \nu_n \quad (12)$$

ν_n depends on the weights p_{nl} defining the average densities of the l-degenerate SHM, Eq.(5). It vanishes if $p_{nl} = (2l+1)/n^2$. In the present work, ν_n has been adjusted to get the best possible results.

The total energy, as given in Eq.(1), still holds with the new charges of Eq.(10). The one-electron energies \mathcal{E}_{nl} are obtained as derivatives of this total energy with respect to subshell populations P_{nl} . We don't give here their detailed expression for brevity, but it can be found elsewhere /2/. Table 1 shows an example of results that are obtained in the SHM with l-splitting.

Table 1 - Comparison of one-electron energies. SHM, degenerate with respect to angular momentum: deg. ; SHM with l-splitting included: l-spl. ; Hartree-Fock Theory: HF /3/. Case of Neon, $Z = 10$. Hartree units. Negative sign omitted everywhere.

<u>state</u>	<u>deg.</u>	<u>l-spl.</u>	<u>HF</u>
1s	33.187	32.802	32.772
2s	0.627	1.917	1.930
2p	0.627	0.833	0.850

The following Figure gives an overall idea of the accuracy of the SHM for total energy calculations.

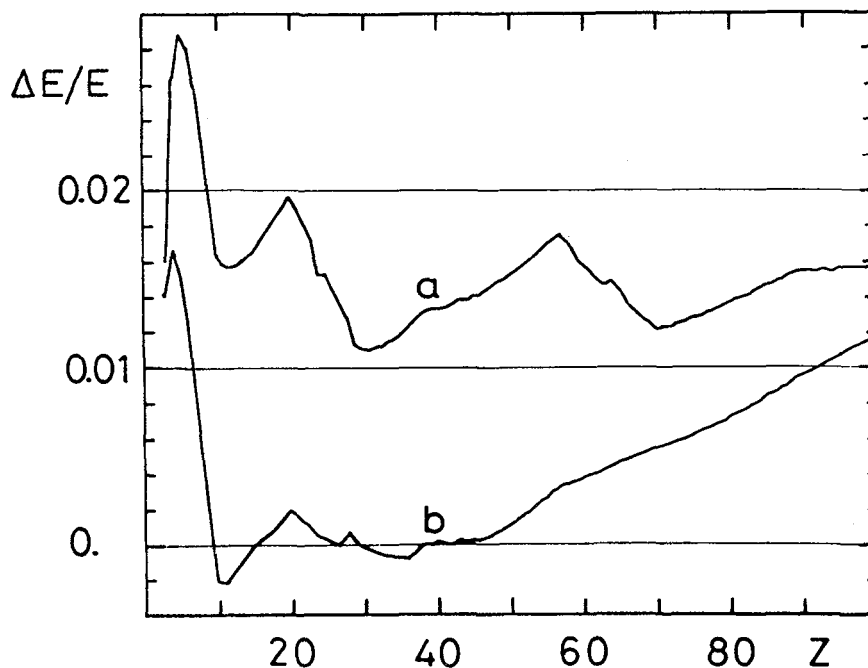


Fig. 1 - Relative difference between the total energies of neutral atoms in their ground state.

$\Delta E/E = (E_{HF}/E_{SHM} - 1)$. E_{HF} is the Hartree-Fock total energy /4/, and E_{SHM} is calculated a) in the l-degenerate model b) in the model with l-splitting.

4 - CONCLUSION

We have presented a very simple way for adding l-splitting in the Screened Hydrogenic Model for electronic structure calculations. The numerical efficiency of the SHM is preserved, and the features of l-splitting are correctly predicted. The numerical results could be further improved by fitting the new constants in order to reproduce existing theoretical data.

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