RAPID COMMUNICATIONS

PHYSICAL REVIEW E VOLUME 55, NUMBER 5 MAY 1997

Hartree-Fock statistical approach to atoms and photoabsorption in plasmas

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(Received 16 August 1996)

Hartree-Fock equations for plasma atoms are proposed and used in the superconfiguration method of photoabsorption calculation. They involve statistical sums, taking into account integer shell occupation numbers and finite temperature effects. These sums are evaluated using electron and hole counting. Their use is also shown to be relevant to the treatment of orbital relaxation in the final states of optical transitions. [S1063-651X(97)50805-1]

PACS number(s): 52.25.−b, 31.15.−p, 78.70.Dm

In this communication we propose a new statistical Hartree-Fock approach to atoms in plasmas at finite temperature. It is based on the superconfiguration approximation successfully applied in the superconfiguration transition arrays method (STA) [1–5] to interpret transmission spectra of low-density plasmas measured in laboratories [1–16].

The original STA method [1–5] is applied in conjunction with the use of parametric potentials calculated by the RELAC code [17] for free ions. In this sense the superconfigurations, as introduced in [1–5], are not fully self-consistent.

The finite temperature Hartree-Fock (HF) method presented here is derived in the framework of the superconfiguration approximation. The average shell populations and interaction matrices are given in terms of statistical sums that are averages of the corresponding quantities for configurations. This allows us to avoid problems stemming from non-integer occupation numbers in other thermal HF theories (see, for instance, discussion in Ref. [14]). The statistical sums appear to be key quantities in all the calculations required by the superconfiguration method: energies, moments of the photoabsorption spectrum.... They are also needed in the relaxation effects described below. The mixed counting (electron or holes), proposed in this work, is applied to HF equations and to all statistical sums in our superconfiguration code.

The superconfiguration contains configurations that are close in energy, i.e., the differences of configuration energies within a superconfiguration are less than kT. The interaction of superconfigurations is neglected. A superconfiguration Ξ is specified by the set of supershell σ populations $\Sigma_{s\in\sigma}q_s^{(C)}=Q_\sigma$, i.e. the sum of the populations in the shells belonging to σ [1]. The superconfiguration of the bound electrons is neutralized by free electrons. The one-electron states are common within each superconfiguration. In thermal equilibrium, assuming that the superconfigurations do not interact, it is sufficient to require that the free energy of each superconfiguration be stationary with respect to its wave functions. The free energy of Ξ is calculated using the configuration-averaged energies of bound electrons and includes a Thomas-Fermi (TF) contribution for the free electrons. In the Boltzmann factor, following [1], we use for the configuration energy (C_b is the bound-electron configuration): $E^{(C_b)}=\Sigma_i q_i^{(C_b)}a_i+\langle E_2^{(C_b)}+E_{bf}^{(C_b)}\rangle_\Xi+F_{ff}^{(\Xi)}$, where only the first linear term depends explicitly on the bound-shell populations $q_i^{(C_b)}$, the other terms being averaged over Ξ. $F_{ff}^{(\Xi)}$ is the free energy of free electrons. In the original STA, it is approximated by $F_f^{(\Xi)}=\mu Z_f^{(\Xi)}$, where μ is the average atom (AA) chemical potential and $Z_f^{(\Xi)}$ the number of free electrons in the superconfiguration. $E_{bf}^{(C_b)}$ is the bound-free interaction energy. $E_2^{(C_b)}$ is the rest of the bound-bound interaction energy quadratic in $q_i^{(C_b)}$ [18,14,19]. Finally, we find that the bound-electron energy, averaged over all configurations in Ξ, may be given a form analogue to the HF energy:

$$\langle E^{(C_b)}\rangle_\Xi-F_{ff}^{(\Xi)}=\sum_r \alpha_r I_r+1/2\sum_{r,s}\alpha_r(\alpha_s-\delta_{r,s})W_{r,s}V_{r,s}. \tag{1}$$

$\alpha_r=p_r g_r$ is the averaged population of the bound-shell r of degeneracy g_r. I_r and $V_{r,s}$ are the one- and two-electron integrals [18,14,19] of Ξ, respectively. α_r and $W_{r,s}$ are given in terms of the relative statistical sums for electrons:

$$A_{\sigma_r,Q_{\sigma_r},n}=U_{\sigma_r,Q_{\sigma_r}-n}(g)/U_{\sigma_r,Q_{\sigma_r}}(g)$$

or for holes:

$$A^*_{\sigma_r,Q^*_{\sigma_r},n}=U^*_{\sigma_r,Q^*_{\sigma_r}-n}(g)/U^*_{\sigma_r,Q^*_{\sigma_r}}(g):$$

$$\begin{aligned} p_r&=-\sum_{n=1}^{Q_{\sigma_r}}(-X_r)^n A_{\sigma_r,Q_{\sigma_r},n}\\ &=\sum_{n=0}^{Q^*_{\sigma_r}}(-X_r^*)^n A^*_{\sigma_r,Q^*_{\sigma_r},n}, \end{aligned} \tag{2a}$$

$$X_r=(X_r^*)^{-1}=\exp(-\beta a_r), \tag{2b}$$

$$\begin{aligned} W_{r,s}=1+\delta_{\sigma_r,\sigma_s}\{&\delta_{r,s}[S_r(g_r-1)/(p_r g_r-1)-1]\\ &+(1-\delta_{r,s})H_{rs}\}, \end{aligned} \tag{3}$$

where $H_{rs}=(X_s-X_r)^{-1}(X_s/p_s-X_r/p_r)-1$ and

$$S_r p_r = \sum_{n=1}^{Q_{\sigma_r}} (n-1)(-X_r)^n A_{\sigma_r, Q_{\sigma_r}, n}$$
$$= \sum_{n=0}^{Q^*_{\sigma_r}} (n+1)(-X^*_r)^n A^*_{\sigma_r, Q^*_{\sigma_r}, , n} . \qquad (4)$$

σ_r denotes the supershell to which r belongs. g denotes the ensemble of degeneracies of the shells. $U_{\sigma,Q}(g)$ and $U^*_{\sigma,Q^*}(g)$ are statistical sums of electrons and holes, respectively. $U_{\sigma,Q}(g)$ was introduced by Bar-Shalom *et al.* in Ref. [1] and $U^*_{\sigma,Q^*}(g)$ will be defined below. From Ref. [1] one has

$$U_{\sigma,Q}(g) = \sum_{\substack{q_s, \Sigma q_s = Q \\ s \in \sigma}} \prod_{s \in \sigma} \begin{pmatrix} g_s \\ q_s \end{pmatrix} X_s^{q_s}.$$

It can be calculated in Q steps using recurrent relations [1]. We found that, in the case of supershells having a large number of bound electrons, it is necessary to replace in statistical sums, the electron counting by the hole counting. The number of holes is $Q^* = G_\sigma - Q$, where $G_\sigma = \Sigma_{s \in \sigma} g_s$ is the total degeneracy of the supershell σ. We define the statistical sum of holes as follows:

$$U_{\sigma,Q}(\{g_s, X_s; s \in \sigma\}) = U^*_{\sigma,Q^*}(\{g_s, X^*_s; s \in \sigma\}) \prod_{r \in \sigma} X_r^{g_r}. \quad (5)$$

The formal dependence of $U^*_{\sigma,Q^*}(g)$ on g, Q^*, and X^*_s is the same as in the case of the electron statistical sum. We apply the hole counting in case of supershells such that $Q > G_\sigma/2$. The number of recurrent operations is then lower in hole counting and moreover, this choice guarantees the numerical accuracy in the recurrent relations.

The stationarity condition with the usual assumption of the wave-functions orthonormality leads to the following set of self-consistent-field (SCF) equations (in atomic units, all subscripts referring to superconfiguration are omitted for simplicity):

$$(\hat{K}_m + V(r) + \delta V_m(r) - \epsilon_m) P_m(r) + h_m(r)$$
$$= \sum_{k \neq m} \epsilon_{m,k} \alpha_k \delta_{l_m, l_k} P_k(r), \qquad (6a)$$

where $P_m(r)/r$ is the radial wave function, $\hat{K}_m$ the kinetic energy operator, ϵ_m appears as the normalization Lagrange multiplier, and the matrix $\epsilon_{m,k}$ as the orthogonality multipliers. The SCF potential of the superconfiguration is

$$V(r) = \int d\mathbf{r}' [\rho_b(r') + \rho_f(r')] / |\mathbf{r} - \mathbf{r}'| - Z/r. \qquad (6b)$$

$\rho_f(r)$ and $\rho_b(r) = \Sigma_s \alpha_s |P_s(r)|^2/(4\pi r^2)$ are the free and bound spherical electron densities, respectively. The correction to the potential and the nonhomogeneous term are

$$\delta V_m(r) = \sum_s \delta_{\sigma_m, \sigma_s} \sum_k \{\delta_{m,s}(g_m - 1)[g_m(S_m - p_m)\delta_{k,0}$$
$$- S_m] + (1 - \delta_{m,s}) \alpha_s H_{ms} \delta_{k,0}\} Y^{(k)}_{s,s}(r), \qquad (6c)$$

$$h_m(r) = -\sum_{s \neq m} \alpha_s [\delta_{\sigma_m, \sigma_s} H_{ms} + 1] P_s(r) \sum_k Y^{(k)}_{s,m}(r), \qquad (6d)$$

where

$$Y^{(k)}_{s,m}(r) = \frac{g_m}{2(g_m - \delta_{s,m})} \begin{pmatrix} l_m & k & l_s \\ 0 & 0 & 0 \end{pmatrix}^2$$
$$\times \int_0^\infty dr' \frac{r_<^k}{r_>^{k+1}} P_s(r') P_m(r'). \qquad (6e)$$

If there is only one shell in a supershell or if a supershell is closed, the equations reduce to the usual HF equations [14,18]. If a supershell contains only one electron, the equation for each shell belonging to the supershell is of the HF form as if the other shells were unoccupied. If the subdivision of superconfigurations is increased, we get in the limit the restricted HF SCF equations of detailed configuration accounting (DCA). In this limit, neglecting the free-electron effects, one gets [14]

$$a_m = \frac{d}{d\alpha_m} \langle E_b^{(C_b)} \rangle_\Xi = \epsilon_m + (1/2) V_{m,m} . \qquad (7)$$

We use the second identity of Eq. (7) in the general case in order to specify a_m in Eq. (2b).

The probability $\exp(B^{(\Xi)})$ of a superconfiguration Ξ can be expressed using:

$$B^{(\Xi)} = \ln(U^{(\Xi)}) - B_2^{(\Xi)}$$
$$= \ln(U^{(\Xi)}) - \beta(\langle E_2^{(C_b)} + E_{bf}^{(C_b)} \rangle_\Xi + F_{ff}^{(\Xi)}), \qquad (8)$$

where $U^{(\Xi)} = \Pi_{\sigma \in \Xi} U_{\sigma, Q_\sigma}(g)$ is the statistical sum of Ξ. The difference of the $B^{(\Xi)}$ in two superconfigurations measures their relative probability. We illustrate some consequences of the present theory by comparing values of $B^{(\Xi)}$ obtained making different assumptions, in the case of three superconfigurations of Germanium at temperature $T = 68$ eV and at 0.05 g/cm^3 density [7,3]. The results are presented in Table I. The most probable superconfiguration, when $n = 3$ and $n = 4$ shells are grouped together, is $\Xi_0 = (1s)^2(2s)^2(2p)^6(3s3p3d)^7(4s4p4d4f)^2$, the second with different ionic charge is $\Xi_1 = (1s)^2(2s)^2(2p)^6(3s3p3d)^7(4s4p4d4f)^3$ and the third one is $\Xi_2 = (1s)^2(2s)^2(2p)^6(3s3p3d)^8(4s4p4d4f)^1$ (same charge as Ξ_0). The results are presented in Table I. In each thermodynamic model [(a): superconfiguration neutralized by $Z_f^{(\Xi)} = Z - \Sigma_\sigma Q_\sigma$ free electrons, (b): free ion and AA chemical potential $F_f^{(\Xi)} = \mu Z_f^{(\Xi)}$ in Eq. (8)], we compare $\Delta B_{1,0} = B^{(\Xi_1)} - B^{(\Xi_0)}$ and similarly $\Delta B_{2,0}$, obtained with $a_m = \epsilon_m$ or with a_m given by Eq. (7), and using $B_2^{(\Xi)}$ calculated with and without temperature. One observes that the neglect of the thermal effects in the superconfiguration average of the term $B_2^{(\Xi)}$, proposed in Ref. [1], is justified. The inclusion of the correction $(1/2)V_{m,m}$ in Eq. (2b) leads us

TABLE I. Comparison of relative probabilities (with respect to Ξ_0) in case of superconfigurations Ξ_1 and Ξ_2.

	Thermodynamic model	$T=68$ eV in $B_2^{(\Xi)}$, $a_m=\epsilon_m+\frac{1}{2}V_{m,m}$	$T=68$ eV in $B_2^{(\Xi)}$, $a_m=\epsilon_m$	$T=0$ in $B_2^{(\Xi)}$, $a_m=\epsilon_m$
$\Delta B_{1,0}$	(a) with free electrons	2.485	2.620	2.620
$\Delta B_{2,0}$		3.225	3.368	3.357
$\Delta B_{1,0}$	(b) free ion model	2.968	3.103	3.104
$\Delta B_{2,0}$		3.222	3.365	3.354

also to relatively small differences. The differences between results from the SCF model, taking into account the free electrons and the results from the free ion model, are large in the case of $\Delta B_{1,0}$. This is due to the fact that Ξ_0 and Ξ_1 have different $Z_f^{(\Xi)}$. In the case of $\Delta B_{2,0}$, i.e., superconfigurations of equal $Z_f^{(\Xi)}$, both approaches to thermodynamics give practically the same results. In that case we observed also similar agreement of other physical quantities. Especially the positions of the absorption structures are not al-

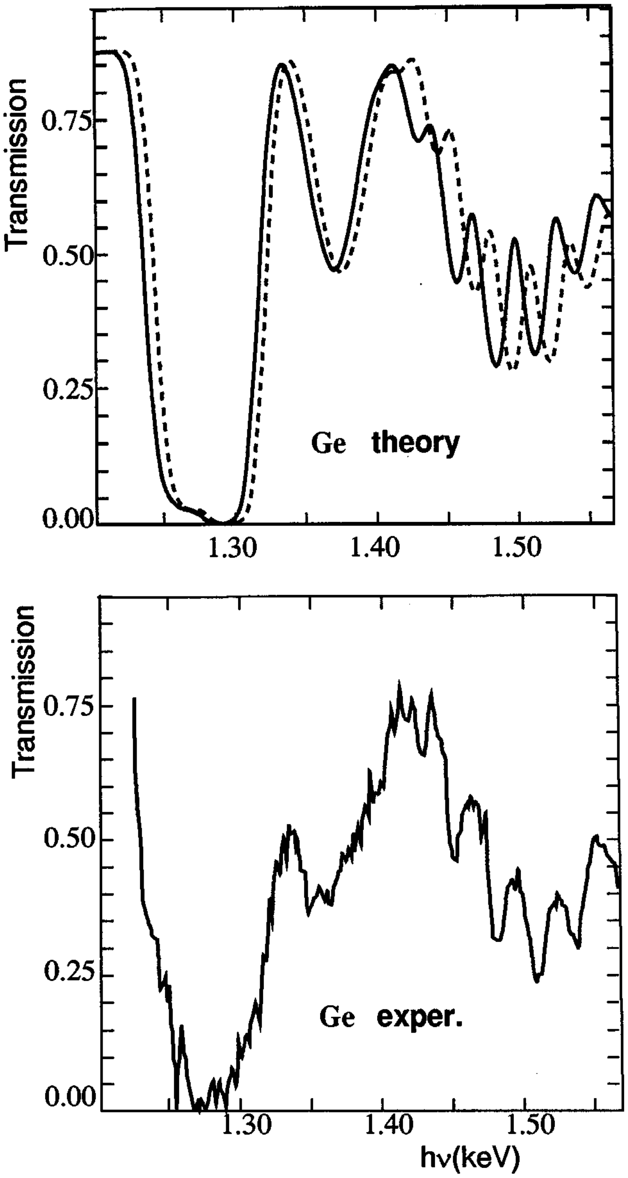

FIG. 1. Theoretical and measured [6] transmission spectrum of germanium. Calculations at $T=68$ eV and 0.05 g/cm^3 density. — orbital relaxation included; - - - without orbital relaxation.

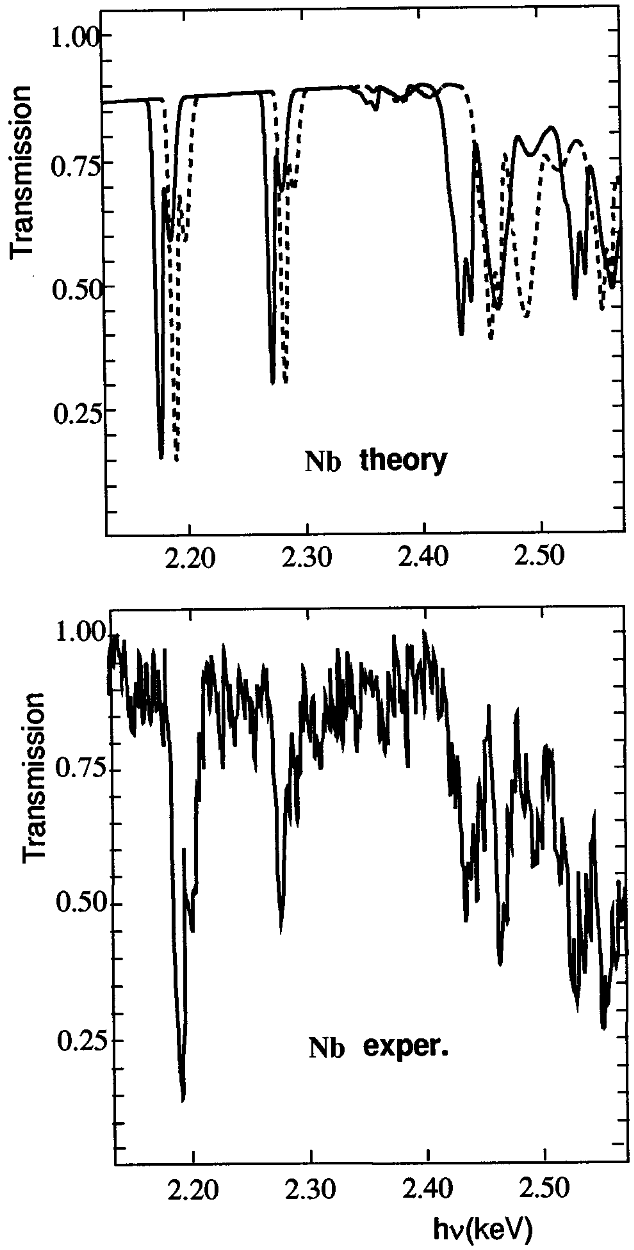

FIG. 2. Theoretical and measured [11] transmission spectrum of niobium. Calculations at $T=47$ eV and 0.017 g/cm^3 density. — orbital relaxation included; - - - without orbital relaxation.

tered by changes in thermodynamics. The differences on the relative strength of the bound-bound absorption structures between models (a) and (b) in the case of $\Delta B_{1,0}$ are probably due to the use of the AA chemical potential.

As described above we use wave functions self-consistently calculated in each superconfiguration. In the original STA papers, this use of different sets of orbitals, obtained from the RELAC code, is called ''orbital relaxation'' [4]. In connection with photoabsorption calculations, we reserve the words ''orbital relaxation'' for the use of different orbitals in the initial and final superconfigurations involved in an optical transition. The HF estimate of the correction to the $\alpha\rightarrow\beta$ transition frequency, due to relaxation, is

$$\Delta E_C^{\alpha\rightarrow\beta}=\Delta I_\beta+\tfrac{1}{2}\sum_i\,(q_i^{(0)}-\delta_{i,\alpha})(2\Delta V_{\beta,i}-\Delta V_{i,i}+2\Delta I_i)+\tfrac{1}{2}\sum_{ij}\,(q_i^{(0)}-\delta_{i,\alpha})(q_j^{(0)}-\delta_{j,\alpha})\Delta V_{i,j}\,. \qquad (9)$$

$\Delta I_i=I_i-I_i^0$ is the difference between the final and initial one-electron integrals, and $\Delta V_{i,j}$ is the similar difference for the two-electron integrals. The $q_i^{(0)}$ are the shell occupations in the initial configuration. The correction of Eq. (9) does not appear in the published formulas [1–5] although these effects might be modeled in a different manner (for instance by a global shift in frequency, as in Ref. [11]). While the unrelaxed frequency has only linear dependence on the populations, Eq. (9) includes a quadratic term. Such quadratic terms are present in the expression of the variance of the transition array, with a product of vectors D_iD_j [1,3] instead of the matrix $\Delta V_{i,j}$. This does not affect the technique of averaging, so that all the machinery related to the statistical sums needed in the evaluation of the variances can be adapted to the relaxation correction of the frequency. We do not include relaxation corrections in the zero-order and second-order moments of the transition array.

Figures 1 and 2 present comparison between calculated and measured transmission spectra in the cases of germanium of Ref. [7] and of niobium at $T=47$ eV and at 0.017 g/cm^3 density [11]. Relativistic and orbital relaxation effects in the final superconfiguration, as described above, have been included in these calculations. The comparison with theoretical spectra calculated without orbital relaxation effects in Ge and Nb shows that these effects are important in the interpretation of experiments, as already noticed [11]. The SCF HF calculations of final superconfigurations are thus necessary. A more detailed description of the relaxation correction to the first moment of the photoabsorption cross section will be given elsewhere.

In conclusion, we propose statistical Hartree-Fock self-consistent equations for partially ionized plasmas in the approximation of superconfigurations. The theory takes into account the effects of finite temperature and of integer shell occupation numbers respecting the Pauli principle. Exact form of the exchange term is preserved. The theory converges to the HF SCF equations for configurations in case of supershells composed of only one shell. The practical implementation of this theory requires only straightforward modifications of existing HF codes and can be easily generalized to HF-Dirac equations. The statistical sums, which are the key quantities in this approach, must be accurately computed using the mixed counting. The formulas for hole counting are given in this communication. Application of this theory to final-state relaxation is shown.

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