Further stable methods for the calculation of partition functions in the superconfiguration approach

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The extension to recursion over holes of the Gilleron and Pain method for calculating partition functions of a canonical ensemble of noninteracting bound electrons is presented as well as a generalization for the efficient computation of collisional line broadening.

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I. INTRODUCTION

In plasmas, supertransition-array (STA) methods are often used to compute the emission and opacity of intermediate to high-Z elements where detailed configuration accounting methods would be prohibitively expensive [1,2]. The STA method requires the calculation of independent electron partition functions under the constraint that the total occupation of a group of spin orbitals (referred to as a supershell) has an integer occupation.

For large supershells and/or low temperatures, efficient recursion relations for generating these partition functions suffer from numerical instability due to precision cancellations involving sums of large terms of alternating sign [3]. Recently a slightly less efficient algorithm has been advanced which, however, does not suffer from numerical instabilities [4]. It is based upon computing partition functions by nested recursion—building up supershells one spin orbital at a time—at each stage from "parent" supershells (of one less spin orbital) with smaller occupation values. By definition all terms entering the sums of this recursion are positive definite, and so cancellation errors are avoided.

However, for large supershells that are nearly closed (have few vacancies or holes) this algorithm is needlessly inefficient, as the partition function must be built by adding electrons from an empty supershell up to the nearly full occupation. An alternative stable algorithm is easily constructed which consists of building the partition function by adding *holes* to a completely filled supershell, and requires far fewer steps for nearly closed supershells. It is presented here for completeness, and also as a useful independent check on current algorithms.

II. A RECURSION FROM FULL SHELLS

The development here closely follows that of Gilleron and Pain. Our objective is to compute the supershell partition function at (inverse) temperature $\beta=1/kT$,

$$U_Q^{[n]} = \sum_{|\vec{p}|=Q} e^{-\beta\Omega(\vec{p})}, \tag{1}$$

where the sum runs over all $\vec{p}$ configurations containing Q electrons. This constraint is denoted as $|\vec{p}|=\Sigma_{i=1}^{n} p_i = Q$ for an n orbital supershell with integer occupations p_i and degeneracy g_i. The thermodynamic potential of our independent electron system (which usually is a reference system for perturbative approaches) is assumed to be

$$\Omega(\vec{p}) = \sum_{i=1}^{n} p_i\varepsilon_i - \frac{1}{\beta}\ln\left\{\prod_{i=1}^{n}\binom{g_i}{p_i}\right\} - \mu Q. \tag{2}$$

From the definition of the generating function [5],

$$F(z) \equiv \sum_{Q=0}^{G^{(n)}} z^{G^{(n)}-Q} U_Q = \prod_{i=1}^{n} \{z + X_i\}^{g_i}, \quad X_i \equiv e^{-\beta\{\varepsilon_i-\mu\}}, \tag{3}$$

it follows that the partition function for $Q=G^{(n)}-h$ number of electrons is given by

$$U_{G^{(n)}-h}^{[n]} = \left.\frac{1}{h!}\left(\frac{\partial}{\partial z}\right)^h F(z)\right|_{z=0}, \tag{4}$$

where h denotes the number of holes and the n-orbital supershell degeneracy is $G^{(n)}=\Sigma_{i=1}^{n} g_i$. Using the multiple derivative formula of Leibnitz,

$$\left(\frac{\partial}{\partial z}\right)^q \{AB\} = \sum_{m=0}^{q}\binom{q}{m}\left\{\left(\frac{\partial}{\partial z}\right)^{q-m} A\right\}\left\{\left(\frac{\partial}{\partial z}\right)^m B\right\}, \tag{5}$$

one obtains

$$\begin{aligned} U_{G^{(n)}-h}^{[n]} &= \sum_{m=0}^{h}\left\{\frac{1}{(h-m)!}\left(\frac{\partial}{\partial z}\right)^{h-m}\prod_{i=1}^{n-1}\{z+X_i\}^{g_i}\right\} \\ &\quad\times\left\{\frac{1}{m!}\left(\frac{\partial}{\partial z}\right)^m \{z+X_n\}^{g_n}\right\}\Bigg|_{z=0} \\ &= \sum_{m=\max[0,h-G^{(n-1)}]}^{\min[h,g_n]} U_{G^{(n-1)}-h+m}^{[n-1]}\binom{g_n}{m} X_n^{g_n-m}, \end{aligned} \tag{6}$$

with the degeneracy and partition function of the parent ($n-1$ orbital) supershell denoted $G^{(n-1)}=\Sigma_{i=1}^{n-1} g_i$ and $U_Q^{[n-1]}$, respectively. Similar to the recursion relation based upon building up electrons [Eq. (26) of Ref. [4]] we initialize the present recursion over holes from the no-orbital partition function values

$$U_Q^{[0]} = \delta_{Q,0}. \tag{7}$$

However, with the present relation only nh [in contrast to $n(G^{(n)}-h)$] steps are required, and so is preferred for nearly closed shells.

III. VARIATIONS ON A THEME

The general approach of Gilleron and Pain (recursion over orbitals as well as electrons and/or holes) introduces a flexibility that allows for the efficient specialization of algorithms requiring partition functions. In this section we consider the computation of supertransition-array collisional line broadening as an illustration.

The Lorentzian full width of a transition line is proportional to the decay rates of the initial and final configurations involved in the transition. Let us consider electron impacts in the dipole approximation.

Collisional excitation rates (s^{-1}) from a detailed configuration "c" (a vector of integer orbital occupations $c \equiv \{n_1, n_2, \ldots\}$) by an electron jumping from a lower orbital "l" to an upper orbital "u" are given by (e.g.) Van Regemorter's formulas [6]

$$\Gamma^c_{l\to u} = \frac{1}{2} N_e \lambda^3 \frac{E_h}{2\pi\hbar} \frac{8\pi}{\sqrt{3}} n_l^c \{g_u - n_u^c\} \frac{f^c_{l\to u}}{g_u} \frac{e^{-\Theta_\uparrow}}{\Theta_\uparrow} f_{\mathrm{Gaunt}}(\Theta_\uparrow),$$

$$\Theta_\uparrow = \frac{E^{c-1_l+1_u} - E^c}{kT}, \tag{8}$$

while the formula for deexcitation rates from configuration "c" is

$$\Gamma^c_{u\to l} = \frac{1}{2} N_e \lambda^3 \frac{E_h}{2\pi\hbar} \frac{8\pi}{\sqrt{3}} \{g_l - n_l^c\} n_u^c \frac{f^c_{u\to l}}{g_l} \frac{1}{\Theta_\downarrow} f_{\mathrm{Gaunt}}(\Theta_\downarrow),$$

$$\Theta_\downarrow = \frac{E^c - E^{c-1_u+1_l}}{kT}. \tag{9}$$

Here

$$\lambda = \left\{ \frac{2\pi\hbar^2}{mkT} \right\}^{1/2}, \quad E_h = \frac{\hbar^2}{m a_0^2} = 27.2116 \text{ eV} \tag{10}$$

and we have denoted a configuration vector with occupation unity in the ith orbital and zero elsewhere as 1_i. The Gaunt factor typically is given as a semiempirical expression, for example,

$$f_{\mathrm{Gaunt}}(\Theta) = \begin{cases} (\sqrt{3}/2\pi)(1+\Theta)(-\ln\Theta - \gamma + \Theta), & \Theta \leqslant 0.4, \\ 0.200 + 0.282\,978\,3 e^{-3\Theta}, & \Theta > 0.4, \quad \Theta = \dfrac{\Delta E}{kT}, \end{cases} \tag{11}$$

as taken from Sobelman [7]. Detailed balance is ensured by the following relation among effective one-electron oscillator strengths:

$$g_l f^{c_i}_{l\to u} = g_u f^{c_f}_{u\to l}, \quad c_f = c_i - 1_l + 1_u, \tag{12}$$

which in the independent electron framework is equivalent to neglecting orbital relaxation in the dipole matrix element

$$g_l f^{c_i}_{l\to u} = g_u f^{c_f}_{u\to l} = \frac{1}{3} \frac{E^{c_f} - E^{c_i}}{\frac{1}{3}E_h} |\langle l \| D \| u \rangle|^2. \tag{13}$$

The extension to superconfiguration accounting is obtained by averaging the above expressions over all detailed configurations (Boltzmann weighted) allowed within the superconfiguration Ξ. For collisional excitations we obtain

$$\Gamma_{l\to u} = \frac{1}{2} n_e \lambda^3 \frac{E_h}{2\pi\hbar} \frac{8\pi}{\sqrt{3}} \langle n_l \{g_u - n_u\} \rangle_\Xi \frac{f_{l\to u}}{g_u} \frac{e^{-\langle \Delta E \rangle_\Xi / kT}}{\left(\dfrac{\langle \Delta E \rangle_\Xi}{kT} \right)} \langle f_{\mathrm{Gaunt}} \rangle_\Xi. \tag{14}$$

Note that this formula already contains approximations in which correlated quantities are assumed to be uncorrelated, but their correction is generally subsumed into the definition of the approximant Gaunt factor. Here our attention will be focused on the oft further taken approximation

$$\langle n_l \{g_u - n_u\} \rangle_\Xi \cong \langle n_l \rangle_\Xi \{g_u - \langle n_u \rangle_\Xi\}. \tag{15}$$

This is usually done to avoid the computational burden of computing supershell correlated averages by traditional recursion relation methods, but does not hold when "l" and "u" are in the same supershell, and leads to violations of Kirchoff's relation when comparing emission and absorption spectra in local thermodynamic equilibrium.

We thereby look to efficiently evaluate correlated averages, for any two distinct orbitals $\alpha \neq \beta$ in the same supershell, starting from the exact formula [8]

$$\begin{aligned} \langle n_\alpha (g_\beta - n_\beta) \rangle &= g_\alpha X_\alpha g_\beta \frac{U_{Q-1}[\vec{g} - \vec{1}_\alpha - \vec{1}_\beta]}{U_Q[\vec{g}]} \\ &= \langle n_\alpha \rangle \left\{ g_\beta \frac{U_{Q-1}[\vec{g} - \vec{1}_\alpha - \vec{1}_\beta]}{U_{Q-1}[\vec{g} - \vec{1}_\alpha]} \right\} \\ &= \langle n_\alpha \rangle \left\{ g_\beta - \frac{g_\beta X_\beta}{X_\beta + \phi} \right\} \\ &= \left\{ \frac{g_\alpha X_\alpha}{X_\alpha + \hat{\phi}} \right\} \{ g_\beta - \langle n_\beta \rangle \}, \end{aligned}$$

$$\phi = \frac{U_{Q-1}[\vec{g} - \vec{1}_\alpha - \vec{1}_\beta]}{U_{Q-2}[\vec{g} - \vec{1}_\alpha - \vec{1}_\beta]},$$

$$\hat{\phi} = \frac{U_Q[\vec{g} - \vec{1}_\alpha - \vec{1}_\beta]}{U_{Q-1}[\vec{g} - \vec{1}_\alpha - \vec{1}_\beta]}. \tag{16}$$

The last forms are reminiscent of Fermi factors, and depend on partition functions with formally and artificially reduced orbital degeneracies. To compute linewidths we must recompute ϕ (or $\hat{\phi}$) for all (dipole allowed) α, β combinations, and this can be inefficient if one builds from scratch the partition

functions for each altered set of orbital degeneracies by the algorithm of Gilleron and Pain. A more efficient procedure employs

$$U_Q[\vec{g}-\vec{1}_\alpha]=\lim_{z\to 0}\frac{1}{Q!}\left(\frac{\partial}{\partial z}\right)^Q F[\vec{g}-\vec{1}_{all}]H^{(\alpha)},$$

$$\vec{1}_{all}\equiv\{1,1,1,\ldots\}, \tag{17}$$

where

$$F[\vec{g}-\vec{1}_{all}]=\prod_{s=1}^{N}(1+zX_s)^{g_s-1}, \tag{18}$$

$$H^{(\alpha)}=\prod_{\substack{s=1\\ s\neq\alpha}}^{N}(1+zX_s). \tag{19}$$

Notice that $H^{(\alpha)}$ is a polynomial in z of order $N-1$ (N the number of subshells in the supershell). This leads to

$$U_Q[\vec{g}-\vec{1}_\alpha]=\sum_{j=0}^{\min[Q,N-1]}U_{Q-j}[\vec{g}-\vec{1}_{all}]h_j^{(\alpha)},$$

$$h_j^{(\alpha)}=\lim_{z\to 0}\frac{1}{j!}\left\{\left(\frac{\partial}{\partial z}\right)^j H^{(\alpha)}\right\}. \tag{20}$$

Furthermore we have

$$U_Q[\vec{g}-\vec{1}_\alpha-\vec{1}_\beta]=\sum_{j=0}^{\min[Q,N-2]}U_{Q-j}[\vec{g}-\vec{1}_{all}]h_j^{(\alpha,\beta)}, \tag{21}$$

$$h_j^{(\alpha\beta)}=\lim_{z\to 0}\frac{1}{j!}\left\{\left(\frac{\partial}{\partial z}\right)^j H^{(\alpha\beta)}\right\},\quad H^{(\alpha\beta)}\equiv\prod_{\substack{s=1\\ s\neq\alpha\\ s\neq\beta}}^{N}(1+zX_s). \tag{22}$$

The efficiency comes from precomputing $U_{Q-j}[\vec{g}-\vec{1}_{all}]$ by Gilleron and Pain's method (or the recursion over holes presented here) and storing the results. The $h_j^{(\alpha)}$ and $h_j^{(\alpha,\beta)}$ coefficients are trivially computed on demand. For example, $h_j^{(\alpha)}$ is obtained by an $N-1$ (number of subshells in the supershell minus one) step array update

$$h_j^{(\alpha)}\leftarrow h_j^{(\alpha)}+X_m h_{j-1}^{(\alpha)},\quad m=0,N,\quad m\neq\alpha, \tag{23}$$

performed using in-place memory (i.e., separate input and output arrays are not needed in their generation) having initialized the vector as $h_j^{(\alpha)}=\delta_{j,0}$.

IV. CONCLUSIONS

The generalization to recursion over holes in lieu of electrons in the method of Gilleron and Pain, alluded to in their paper, is presented here in detail. The generality and utility of their approach has been applied toward efficiently calculating correlated population averages, making feasible studies on the sensitivity of Rosseland mean opacities due to various approximations in collisional line broadening.

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