Formation of composites in equilibrium plasmas

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A generalized, multielectron version of the Planck-Larkin convergent hydrogenic partition function is presented. It is shown that compensation between bound and scattering states leads naturally to convergent expressions for multielectron bound-state partition functions. The nature of the compensation is studied by comparing a high-temperature expansion of the bound-state sum with a perturbation expansion in the coupling parameter βe^2 of the complete trace. The analytic form of high-order quantum perturbation terms is determined from a parametrized pseudopotential method. Rigorous evaluation of low-order quantum perturbation expressions is used to determine parameter values.

I. INTRODUCTION

Much of the current literature on equilibrium plasmas is concerned with complete ionization. Frequently the electrons are treated as being highly degenerate, such that they form a nearly uniform background while the heavy ions are classical. This is appropriate to the conditions present in the center of white dwarf stars. For less extreme conditions the electron distribution may be far from uniform and, for kT less than the binding energy, composite particles will be formed. The present work is primarily concerned with how the formation of composite particles affects the statistical mechanical methodology.

Since the grand partition function works with physical clusters it is the natural starting place for treating chemically reacting plasmas. Nevertheless, due to the long-range divergence in each of the cluster coefficients, it is convenient to first find a convergent expression for the Mayer S function,

$$S=-(F-F_0)/VkT, \tag{1}$$

where F and F_0 are the Helmholtz free energies for the interacting and noninteracting system, respectively. It was shown in a previous paper,[1] hereafter referred to as I, that the grand canonical partition function can be generated from derivatives of S, i.e., a convergent activity (fugacity) expression for S in the canonical formulism can be used to generate a convergent grand canonical partition function. The activity expression that is obtained is not properly ordered to handle the formation of physical clusters and must first be reorganized into a cluster expansion before progress can be made. This is described in the sequel[2] to I, hereafter referred to as II, and elsewhere.[3] The resulting cluster expansion is still not properly normalized since the formation of bound states for $kT<|E_b|$, the binding energy, lowers the order of the cluster coefficients. For example, due to its exponential temperature dependence the bound-state part of the electron-ion second cluster coefficient $b_{e\alpha}$ enters the cluster expansion like a new ideal particle, while the continuum-state part enters like a real two-body interaction between electrons and ions. Because of this it is necessary to introduce an augmented set of activity variables such that the leading term in the revised activity series corresponds to the Saha ionization equilibrium equation.[2,4,5] Scattering states only appear in the interaction corrections of the properly ordered activity series, i.e., proper treatment of bound clusters requires the decomposition of the trace into bound and scattering parts.

Since the sum over bound states for electron-ion interactions diverges even the Saha, zero coupling, limit presents some difficulties. It is obvious that particles in large orbits are essentially free and various mechanisms for limiting the bound-state sum have been introduced. The renormalization of the grand partition function just described works with the complete trace, so that some latitude in how one defines a composite particle is afforded. An improper decomposition will ultimately be rectified through high-order terms. However, since in general only a few low-order terms will be evaluated, a physically realistic decomposition must be made. One of the main purposes of this paper is to show that the well known compensation between bound and scattering states leads naturally to a proper decomposition procedure. The resulting effective bound-state sum is convergent and there is no need to invoke any cutoff criteria. The other purpose of this paper is to study the general form of the quantum perturbation expansion.

It has been shown,[6] in the semiclassical approximation, that the high-temperature expansion of the two-body bound-state partition function involves integrals over $(-V/kT)^{s+3/2}$, $s=0$, 1, 2, etc., which are completely compensated by similar

terms in the scattering-state partition function. Bolle and Smeesters[7] have recently studied this compensation using the theory of time delay in scattering. Due to the compensation the total partition function only involves $(-V/kT)^{s+1}$ and is analytically similar to the partition function for repulsive potentials. It will be shown that those terms in the high-temperature expansion of the bound-state sum that can be treated by integral approximation always compensate with scattering terms. It follows that the divergent terms in the high-temperature bound-state expansion are always compensated by the scattering-state contribution and should not appear in the properly separated parts of the trace. It will be shown that this is a general result valid for all cluster coefficients. This will be demonstrated for the Debye potential

$$V_{e\alpha} = \xi_e \xi_\alpha e^{-r/D}/r \,, \tag{2}$$

where ξ_i is the charge on species i and D is a screening parameter. The Debye potential is especially well suited for this study, since (i) it approaches a Coulomb potential as D is increased and (ii) a many-body summation of similar types of diagrams, e.g., the ring diagrams, and passing to the limit $D \to \infty$, replaces D with the Debye length which is given by

$$\lambda_D = \left(4\pi\beta \sum_i \xi_i^2 \chi_i\right)^{1/2} , \tag{3}$$

where $\chi_i = \rho_i$ is the density of species i in the canonical formulism and

$$\chi_i = z_i = (2s_i + 1)\lambda_i^{-3} e^{\mu_i/kT} \tag{4}$$

is the activity of species i in the grand canonical formulism. In Eq. (4) s_i is the particle spin,

$$\lambda_i = (2\pi\hbar^2/m_i kT)^{1/2}$$

is the thermal de Broglie wavelength, and μ_i is the chemical potential.

This paper will improve and extend some of the results of I and II. In particular an improved method of separating the bound- and scattering-state terms is established. An important result of this analysis will be a pseudopotential procedure for generating high-order perturbation terms for the cluster coefficients of the Debye potential. Specific results for the second and third cluster coefficients are given—albeit with some degree of approximation. Furthermore, it is shown that with simple substitutions in the few-body expressions for the Debye potential, it is possible to generate the corresponding many-body perturbation result for the Coulomb limit.

In Sec. II the analytic properties of the second cluster (virial) coefficient for the Debye potential are studied. This is done in two steps. First, semianalytic fits to screening-dependent terms in the high-temperature expansion of the Boltzmann sum for bound states are obtained. Second, using a pseudopotential procedure to extend the known perturbation results for the complete two-body trace, it is shown that terms involving fractional powers of D that arise in the high-temperature bound-state expansion are not present in the complete result, i.e., they have compensated with scattering terms. In Sec. III the process is repeated for three-body states and a convergent bound-state partition function, resulting from compensation with scattering states, is obtained. Analysis of the ring diagrams, for all orders, including Fermi and Bose statistics is given. In addition, explicit perturbation results for both the few-body problem and the Coulomb problem are given through sixth order in $\beta\xi^2$. These results can be applied to either the density or the activity expansions using expressions developed in I and II.

II. ANALYTIC PROPERTIES AND PERTURBATION EXPANSION FOR THE SECOND CLUSTER COEFFICIENT

A. High-temperature bound-state expansion

Expansion of the bound-state part $b^b_{e\alpha}$ of the two-particle cluster coefficient for electrons e and point ions α in powers of β gives

$$b^b_{e\alpha}(4\pi^{3/2}\lambda^3_{e\alpha})^{-1} \equiv Q_{e\alpha} = \sum_{nl} (2l+1)e^{-\beta E_{nl}} = \sum_{m=0}^{\infty} \omega_s \beta^s \,, \tag{5a}$$

where s is the perturbation order,

$$\omega_s = \sum_{nl} (2l+1) E^s_{nl}/s! \,, \tag{5b}$$

and

$$\lambda_{ij} = \hbar/(2\mu_{ij} kT)^{1/2} \tag{5c}$$

is the thermal de Broglie wavelength divided by $\sqrt{\pi}$ in terms of the reduced mass μ_{ij}. Quantum mechanical expressions for the ω_s are difficult to obtain for general potential forms. Since we are primarily interested in large orbit divergencies the following simiclassical approximation is useful[6]

$$\omega_s = \frac{2^s}{\pi(2m+3)!!} \int_0^\infty dr\, r^2 (-V)^{s+3/2} \,. \tag{5d}$$

The validity of Eq. (5d) depends on the form of the potential. In the case of potentials that have a $1/r$ singularity, e.g., the Debye and Coulomb potentials, only ω_0 and ω_1 converge as $r \to 0$. The functional form of $\omega_s(D)$ can, nevertheless, be obtained by setting $V = 0$ for $r < \epsilon$. The constants in these expressions can be readily evaluated using a perturbation expansion of the $E_{nl}(D)$, in powers of

D^{-1}, for large D and numerical calculations of the energy levels for small D.

The first few ω_s obtained by the procedure just described are

$$\omega_0 = 8d^{3/2}/9(3\pi)^{1/2} - 0.2289\,, \tag{6a}$$

$$\omega_1/R_z = 32d^{1/2}/15(5\pi)^{1/2} - 0.4932\,, \tag{6b}$$

$$\omega_2/R_z^2 = \zeta(2)/2! - 896/105(7\pi d)^{1/2} + 0.9769d^{-1}\,, \tag{6c}$$

$$\omega_3/R_z^3 = \zeta(4)/3! - \zeta(2)d^{-1} + \frac{512}{105d(\pi d)^{1/2}} - 1.2670d^{-2}\,, \tag{6d}$$

where

$$R_z = \hbar^2 Z^2/2\mu_{e\alpha}a_{e\alpha}^2\,,\quad a_{e\alpha} = \hbar^2/e^2\mu_{e\alpha}\,,$$
$$d = ZD/a_{e\alpha} = -(\beta\xi_e\xi_\alpha/2\lambda_{e\alpha}^2)D\,; \tag{6e}$$

$$\zeta(\nu) = \sum_{n=1}^{\infty} n^{-\nu}\,,\quad \zeta(2) = \tfrac{1}{6}\pi^2$$
$$\zeta(4) = \tfrac{1}{90}\pi^4\,,\quad \zeta(\infty) = 1\,. \tag{6f}$$

The fractional power terms in Eqs. (6a)–(6d) all exist in the limit $\epsilon \to 0$ and were obtained directly from Eq. (5d). The terms in $\zeta(s-2)/s!$ are the ω_m for a Coulomb potential, which exist for $s > 1$. The intermediate terms, starting at $s = 3$ and having lower-order D dependence than the fractional power terms, are easily determined from a perturbation expansion of the $E_{nl}(D)$. All terms having a higher-order D dependence than the fractional power term have been approximated by a single term which was chosen to satisfy $\omega_s \to 0$ as $D \to 0.840a_{e\alpha}/Z$, corresponding to the disappearance of all bound states.[8] Equations (6a)–(6d) agree very closely with the numerical results when $D > 4a_{e\alpha}/Z$, but small oscillatory differences exist for $D < 4a_{e\alpha}/Z$.

ω_0 and ω_1 diverge as $D \to \infty$ due to large orbit contributions. However, starting at $s = 2$ the ω_s are largely determined by the ground-state term as shown by the values of $\zeta(\nu)$. It has been shown[6] that ω_0 and the classical part of ω_1, i.e., the term in $(ZD)^{1/2}$, are exactly compensated by scattering-state contributions. The only remaining divergencies are in the scattering-state part of the partition function. After compensation with the continuum the bound-state partition function takes the so called Planck-Larkin form[9-11]

$$Q'_{e\alpha} = \sum_{nl} (2l+1)(e^{-\beta E_{nl}} - 1 + \beta E_{nl})\,. \tag{7}$$

It is important to note that there are additional compensations in $Q'_{e\alpha}$ that will prove to be important in three-body terms, i.e., all the terms involving fractional powers of ZD in Eqs. (6a)–(6d) compensate with scattering terms. This does not significantly affect Eq. (7) since these remaining terms $\to 0$ as $D \to \infty$, even without explicitly introducing the compensation. However, the derivative of $Q'_{e\alpha}$ with respect to D occurs in the three-body problem.[2] To see that there are also compensations, similar to Eq. (7), that occur in the multielectron bound-state partition function, we need to work out the general form of the perturbation expansion, as well as a multielectron generalization of Eqs. (6a)–(6d).

B. Weak-coupling perturbation expansion

The fact that the bound-state part of the second cluster coefficient, Eq. (5a), compensates with the scattering-state part can be verified from a perturbation expansion of the trace, i.e., the complete result is, in some respects, analytically dissimilar to the bound and scattering parts.

Thus far only the first two orders of perturbation theory for $b_{e\alpha}$ have been completely worked out. The higher-order ladder terms have only been obtained in the limit $\gamma'_{ij} = \lambda_{ij}/D \to 0$. The terms for $m < 4$, where m is the perturbation order in powers of βe^2, all diverge as $D \to \infty$ and are given by[12,13]

$$b_{ij}^1 = -2\pi(\beta\xi_i\xi_j)D^2\,,\quad b_{ij}^2 = \tfrac{1}{2}\pi(\beta\xi_i\xi_j)^2 DW(\epsilon_{ij})\,; \tag{8a}$$

$$b_{ij}^3 = \tfrac{1}{3}\pi(\beta\xi_i\xi_j)^3(\ln\gamma'_{ij} + D_q)\,,\quad \gamma'_{ij} \ll 1\,; \tag{8b}$$

where

$$W(\epsilon_{ij}) = 1 + \epsilon_{ij}^2 \sum_{\nu=0}^{\infty} \frac{\epsilon_{ij}^{2\nu}}{(2\nu+1)!!} - \left(\frac{\pi}{2}\right)^{1/2} \epsilon_{ij} e^{\epsilon_{ij}/2}\,, \tag{8c}$$

$$\epsilon_{ij} = \tfrac{1}{2}\gamma'_{ij}\,, \tag{8d}$$

$$D_q = \ln 3 + \tfrac{1}{2}(\gamma_E - 1) = 0.8872\,,\quad \gamma_E = \text{Eulers constant}.$$

For $m \geq 4$ all the perturbation terms converge in the Coulomb limit[10,14]:

$$b_{ij}^m = 2\pi(-\beta)^m \phi_{E,m}/m!\,, \tag{9a}$$

where

$$\phi_{E,m} = \sqrt{\pi}\,\lambda_{ij}^3 \zeta(m-2)(\xi_i\xi_j/2\lambda_{ij})^m m!/\Gamma(m/2+1)\,. \tag{9b}$$

No rigorous quantum perturbation results for $b_{ee\alpha}$, $b_{eee\alpha}$, etc. are available.

The perturbation calculations are difficult and some approximation procedure is necessary to elucidate general properties of high-order diagrams. A frequently used procedure is to introduce a pseudopotential to account for quantum diffraction effects for $r < \lambda$. One of the earliest such potentials, and the easiest to work with, was suggested by Glaubermann and Yukhnovskii[15] for a pure Coulomb potential. It is given by

$$U_{\text{eff}}(r) = \xi_i\xi_j(1 - e^{-Cr/\lambda_{ij}})/r\,, \tag{10}$$

where C is chosen to fit some known analytic result. Kelb has given a more complicated potential,[16] applicable to second order, that keeps the first potential interaction classical but introduces diffraction corrections in the second interaction line. A pseudopotential of the form of Eq. (10) has been used to study diffraction corrections to the pair correlation function.[17]

Care must be taken in applying these pseudopotentials, e.g., only the classical part of the Kelb potential is appropriate in first order, whereas additional modifications are required when a third interaction is turned on. Due to its analytic simplicity, similarity with the Kelb potential,[16] and its appearance in the work of Dunn and Broyles[18] a pseudopotential similar to Eq. (10) will be used here to study general analytic properties of the Debye potential. With inclusion of Debye screening Eq. (10) takes the form

$$U_{\text{eff}}(r, D) = \xi_i \xi_j (e^{-r/D} - e^{-Cr/\lambda_{ij}})/r . \tag{11}$$

The potential of Eq. (11) can only reproduce the first-order result, b^1_{ij} of Eq. (8a) if $C = \infty$, corresponding to the fact that diffraction effects enter at second order. Furthermore the b^2_{ij} result of Eq. (8a) cannot be obtained unless $C \to C(\gamma'_{ij})$. The function $C(\gamma'_{ij})$ that exactly reproduces a particular type of perturbation term can be obtained by assuming, for later use, the general form

$$C = C_{n,m}(\gamma'_{ij}) = h_{n,m} \Big/ \left(1 + \sum_{\nu} a_{n,m,\nu} (\gamma'_{ij})^{\nu}\right) \tag{12a}$$

where n indicates the numbers of particles involved in the interaction, m is the perturbation order for n-particle interactions, and the $h_{n,m}$ and $a_{n,m,\nu}$ are parameters.

In the case of b^2_{ij}, for example, the parameter values are determined by requiring

$$-\pi\beta^2 \int_0^{\infty} dr\, r^2 U^2_{\text{eff}} = b^2_{ij} . \tag{12b}$$

Solving Eq. (12b) for $h_{2,2}$ and the first few $a_{2,2,\nu}$ gives

$$h_{2,2} = 6/\sqrt{\pi} , \tag{12c}$$

$$a_{2,2,1}/h_{2,2} \equiv a'_1 = (4/h^2_{2,2} - \tfrac{1}{2})/3 = -0.050\,311 , \tag{12d}$$

$$a_{2,2,2}/h_{2,2} \equiv a'_2 = (-4/h^3_{2,2} + 8a'_1/h_{2,2} + \tfrac{1}{8}\sqrt{\pi})/3 = -0.000\,158 \tag{12e}$$

$$a_{2,2,3}/h_{2,2} \equiv a'_3 = [4/h^4_{2,2} - 12a'_1/h^2_{2,2} + (4a'^2_1 + 8a'_2)/h_{2,2} - \tfrac{1}{12}]/3 = 0.002\,669. \tag{12f}$$

In the limit $\gamma'_{ij} \to \infty$, $C_{n,m} \to \gamma'_{ij}$, i.e., $U_{\text{eff}} \to 0$. Explicit evaluations of b_2 for the third through sixth order, in βe^2, are given in Appendix A.

Equations (8b)–(8f) and (A1)–(A6) verify that terms in the expansion of the bound-state part of b_{ij}, that involve fractional powers of D, are compensated by continuum-state terms, i.e., the perturbation expansion contains integral power terms similar to those in Eqs. (6a)–(6d), but no fractional power terms. Equation (7) is, therefore, the effective bound-state part of the two-body trace. For $kT > |E_b|$ the perturbation expansion converges fairly rapidly and there is no need to explicitly consider bound states. However, for $kT \ll |E_b|$, $Q'_{e\alpha}$ increases exponentially and completely dominates the trace. The parametric density constraints on the activity expansion of P/kT forces the bound-state part of the two-body cluster term to be of the size of the density of electron-ion composites.[1,2,4,5] As a result, this term enters the cluster expansion as the activity of electron-ion composites, according to

$$z_{e\alpha} = 2 z_e z_\alpha (4\pi^{3/2} \lambda^3_{e\alpha} Q'_{e\alpha}) , \tag{13}$$

where $z_{e\alpha}$, z_e, and z_α are the activities of composites, electrons, and ions, respectively. In the Coulomb problem, since λ_D depends on the activity, $Q'_{e\alpha}$ is also a function of the activity. In order to obtain an ordered expansion in the activity, for which the long-range interaction of composite ions is treated on the same basis as for bare ions, it is necessary to Taylor expand $Q'_{e\alpha}$. This is described in II. The leading screening correction to the Coulomb energy levels is the same size for all levels of a particular type of composite and has the magnitude Ze^2/λ_D (or Ze^2/D in the few-body case). The low-order terms in an ordered activity expansion effectively shift the Debye energy levels, to terms of order λ_D^{-2}, back to the Coulomb limit. For strong coupling of the ion cores to the many-body system, such that most bound states are effectively in the continuum, the Ze^2/λ_D shift in the screened energy levels is moderated by high-order terms. A more complete treatment of these considerations will be given in subsequent work.

C. High-temperature scattering-state expansion

After separation of $z_{e\alpha}$, the remaining part of the two-body term, $2z_e z_\alpha b_{e\alpha}$ comes almost entirely from scattering states and enters the cluster expansion at second order in the activity. The scattering contribution for two-body interactions is given rigorously by the Beth-Uhlenbeck phase shift integral[19] according to

$$2z_e z_\alpha b'_{e\alpha} = z_e z_\alpha (4\pi^{3/2}\lambda_{e\alpha}^3)\left(\frac{1}{\pi}\sum_l (2l+1)\int_0^\infty dp\,\frac{d\delta_l}{dp}\exp(-p^2/2\mu_{e\alpha}kT) - \omega_0 - \omega_1\right) \tag{14a}$$

$$= z_e z_\alpha (4\pi^{3/2}\lambda_{e\alpha}^3)\left(\frac{1}{\pi}\sum_l (2l+1)\int_0^\infty dp\,p\delta_l\exp(-p^2/2\mu_{e\alpha}kT) - \omega_1/kT\right), \tag{14b}$$

where δ_l is the phase shift and p is the relative momentum. The ω_0 and ω_1 terms are subtracted from the phase shifts to account for compensation with bound states. Equation (14b) results from an integration by parts and use of Levinson's theorem.[20] When the pseudopotential of Eq. (11) is used a WKB version of Eq. (14b) can be utilized. The WKB expression can be integrated by parts twice so that ω_1/kT is also identically subtracted from the scattering contribution.[6] The scattering contribution can, alternately, be obtained from the results of this section; using Eq. (6a)–(6d), (8a)–(8c), and (A1)–(A6) according to

$$2z_e z_\alpha b'_{e\alpha} = 2z_e z_\alpha\left(b^1_{e\alpha} + b^2_{e\alpha} + \sum_{m=3}^{\infty} 2\pi(-\beta)^m\phi_m/m! - 4\pi^{3/2}\lambda_{e\alpha}^3\beta^{m/2}\omega_{m/2}\right), \tag{14c}$$

where $\omega_{m/2}\equiv 0$ if $m/2$ is not an integer. Actually Eq. (14c) is properly constructed only in the Coulomb limit. In general, since according to Eq. (6e), $d=(-\beta\xi_i\xi_j/2\lambda_{e\alpha}^2)D$, the $\omega_{m/2}$ should be decomposed and only the parts with the appropriate dependence on the coupling parameter subtracted at a given m.

The only bound-state contribution to Eqs. (14a)–(14c) arises from a small quantum noncompensation of ω_1 in the $b^2_{e\alpha}$ term. In the Coulomb problem the $b^1_{e\alpha}$ term in Eq. (14c) is canceled by electrical neutrality and the uncompensated part of the $b^2_{e\alpha}$ term is separated out and appears in the ring sum. In the large-D limit the scattering contributions for $m=4$, 6, 8, etc. are of opposite sign and have $\frac{1}{2}$ the magnitude of the bound-state contributions. However, as D is decreased bound states move into the continuum and the $\omega_{m/2}$ terms decrease more rapidly in magnitude than the scattering terms. For $D\leq 0.840a_{e\alpha}/Z$ there are no bound states, so that all the $\omega_{m/2}=0$ and direct use of the perturbation expansion is again appropriate. Because of this Eq. (14c) is operationally easier to use than the corresponding equation with the $\omega_{m/2}$ decomposed. Reorganization of the activity series as exemplified by Eqs. (13) and (14a)–(14c), therefore, gives a more general formulism which continuously approaches the original expansion at high temperature or small values of the screening parameter. In the Coulomb problem, in the temperature range where composite particles form, small values of the screening parameter correspond to high density.

III. ANALYTIC PROPERTIES AND PERTURBATION EXPANSION FOR HIGHER CLUSTER COEFFICIENTS

Section II has shown how to incorporate the formation of one-electron composites into the cluster expansion. This is appropriate for hydrogen but, for high-Z plasmas, many electron composites may be formed. This section shows how to separate the higher cluster terms into the appropriate, effectively lower order, composite particle contributions.

Quantum perturbation expansions for the third and higher cluster coefficients are very difficult to carry out in complete detail.[5,21] However, with some approximation at short distance a study of the long-range divergencies can be made. In particular we can study the nature of the compensation between bound and scattering states. The good results obtained with the effective potential in the two-body problem seems to justify its use to elucidate the general analytic character for few-body terms. The nature of the diffraction effects is such, however, that a unique two-body pseudopotential cannot give quantitatively exact results. Following the format of Sec. II we first consider the high-temperature bound-state expansion and then work out the complete perturbation result to show that terms involving fractional powers of D are again missing.

A. Three-body bound-state partition function

Calculations of two-electron bound-state energies to obtain equations similar to (6a)–(6d) would require considerable effort. Since we are primarily interested in compensation of large orbit divergences in the bound-state partition function, a semiclassical approach can be used to elucidate qualitative features. A semiclassical approximation to the two-electron bound-state partition function, similar to Eq. (5a), with the ω_m expressed by Eq. (5d), is given in Appendix B. Expansion of the exponential terms of the resultant expressions, Eq. (B5), in u and w and term by term integration gives the following high-temperature expansion.

$$Q_{ee\alpha} = \frac{4T^3 z}{\pi^2}\int_0^\infty d\tau\,\tau^2\left(\tfrac{1}{3}g^{3/2} + \tfrac{2}{3\cdot 5}g^{5/2} + \chi_1\right) \times \int_\tau^\infty d\rho\,\rho^2\left[\tfrac{1}{3}(g')^{3/2} + \tfrac{2}{3\cdot 5}(g')^{5/2} + \chi_2\right], \tag{15}$$

where T_z is the temperature in Z^2 Ry, $g=-V/T_z$, and $g'=-V'/T_z$. For a Debye interaction between point charges, the potentials V and V' are given by Eqs. (B6) and (B7), respectively. The integral over $(gg')^{3/2}$ is the semiclassical equivalent of Levinson's theorem, i.e., it gives the total number of bound states. The integrals over $g^{s_1+3/2}$ and $(g')^{s_2+3/2}$ have obvious interpretations in terms of the high-temperature expansion of the quantum two-electron bound-state partition function [see Eq. (B1)]. The terms χ_1 and χ_2 lump together all high-order terms that have only close distance divergencies. All the terms in Eq. (15) can be shown to involve the factors $(ZD)^{s_1+3/2}$ and $[(Z-1)D]^{s_2+3/2}$, except the integral over $\chi_1\chi_2$, which diverges as $D\to\infty$. Similar to Eqs. (6a)–(6d) there are fractional power terms in the integral over $\chi_1\chi_2$ which $\to 0$ as $D\to\infty$. The extension of Eq. (15) to include an arbitrary number of bound electrons is straightforward.

In Secs. III B and III C we will show that the divergent large orbit terms of Eq. (15) are not presented in the complete partition function. The corresponding Planck-Larkin form of Eq. (B1) resulting from compensation of bound-state divergencies by continuum-state contributions is apparent. In order to use Eq. (B1) in actual applications it is necessary to at least include Pauli principal effects and spin-spin splitting of the energy levels. Including these effects and averaging over electrostatic and spin-orbit splitting gives the following generalization of Eq. (15), resulting from compensation with the continuum:

$$Q'_{ee\alpha}=\sum_{n_1l_1}(2l_1+1)\left[\exp(-\beta E_{n_1l_1})-1+\beta E_{n_1l_1}\right]\times\sum_{n_2l_2}(2l_2+1)g_{n_1l_1n_2l_2S}\times\left[\exp(-\beta E_{n_1l_1n_2l_2S})-1+E_{n_1l_1n_2l_2S}\right] \tag{16a}$$

subject to $n_2l_2\geq n_1l_1$; where $E_{n_1l_1n_2l_2S}$ is the energy relative to the n_1l_1 state. For nonequivalent electrons

$$g_{n_1l_1n_2l_20}=1,\quad g_{n_1l_1n_2l_21}=3; \tag{16b}$$

and for equivalent electrons

$$g_{n_1on_2o,0}=1/a,\quad g_{n_1on_2o,1}=0; \tag{16c}$$

$$g_{n_1ln_2l,0}=6/a,\quad g_{n_1ln_2l,1}=9/a,\quad a=(2l_1+1)^2. \tag{16d}$$

In Eq. (16a) we have subtracted out completely those terms in the high-temperature expansion, that have a large orbit divergence. This is only valid semiclassically. Corrections due to noncompensation, resulting from quantum and statistical effects in low-lying states similar to those for the sum over βE_{nl} in the two-body case,[6] can be determined from a rigorous quantum-statistical perturbation treatment of the appropriate low-order terms.[2] These corrections will be small and can with no loss of generality, be included with the interactions terms. The perturbation analysis of the present work will be nonrelativistic, primarily limited to Boltzmann particles, and only completely rigorous for the ring diagrams.

B. Analytic properties of the ring diagrams

The most divergent part of each of the multiply connected parts of the b_n, in the limit $D\to\infty$, comes from the ring terms. Diagrammatic procedures for summing these diagrams were given by Montroll and Ward.[22] A more complete analysis has been given by DeWitt.[23] Since the interest here concerns the analytic properties of each of the b_n for the Debye potential, not just the many-body sum in the Coulomb limit, a different approach is taken. By working with the ring part of each b_n it is possible to show that the ring diagrams separate naturally into a many-body part and a few-body part. To show this we calculate each of the ring terms b_n^r explicitly and show that the divergence in those terms that diverge at small k (large r) can be removed by summing over similar terms in each b_n, whereas those terms that diverge at large k (small r) can be added together for a given b_n to obtain a finite result. For Boltzmann particles, the quantum perturbation expression[23] for the b_n, when all the particles on the ring are different, is

$$b_n^r=\frac{-B^r_{ijk\cdots\alpha}}{(n-1)}=\frac{-(-1)^n(4\pi)}{2n(2\pi)^3}\int_0^\infty dk\,k^2\tilde{u}_{ij}\tilde{u}_{jk}\cdots\tilde{u}_{\alpha i}\sum_{t=-\infty}^{t=+\infty}L(X_i^2,2\pi it)L(X_j^2,2\pi it)\cdots L(X_\alpha^2,2\pi it), \tag{17a}$$

where

$$X_i^2=\lambda_i^2k^2,\quad \lambda_i=\hbar/(2m_ikT)^{1/2}=\lambda_{ii}/\sqrt{2} \tag{17b}$$

$$L(X_i^2,2\pi it)=\int_0^1 d\nu\exp[-X_i^2\nu(1-\nu)+2\pi it\nu]=(-1)^t(2/\chi_i)\exp(-X_i^2/4+2\pi it)\int_0^{\chi_i/2}d\omega\exp(\omega^2+2\pi it\omega/X_i), \tag{17c}$$

and

$$\tilde{u}_{ab} = \int_0^\infty d\vec{r}\, u_{ab}(r) e^{i\vec{k}\cdot\vec{r}} \tag{17d}$$

is the Fourier transform of the pair potential, and n is the number of particles, designated by $ijk\cdots$ in the cluster. The $t=0$ component of Eq. (17c) involves $\mathrm{Erf}i(X/2)$ so that $L(x^2,0)$ has the expansion

$$L(X^2,0) = \sum_{s=0}^{\infty} a_s X^{2s}, \quad a_s = \frac{(-1)^s}{2^s(2s+1)!!}. \tag{18}$$

The expansion of $L(X^2, 2\pi i t)$ is somewhat more complicated.[23] The first few terms are

$$L(X^2, 2\pi i t) = \frac{1}{(\pi t)^2}\left(\frac{X^2}{2}\right) - \frac{3}{(\pi t)^4}\left(\frac{X^2}{2}\right)^2 + \cdots. \tag{19}$$

Since the analysis is essentially the same when $ijk\cdots$ are all the same, except the results can be stated more concisely, we will generally work with the one-component case.

Substitution of Eqs. (18) and (19) into Eq. (17a) shows that at each n there are $n-2$ terms, having k dependence according to $k^{-2}, k^{-4}, \ldots, k^{-(2n-4)}$, which arise solely from $L(X^2,0)$. These terms are all integrable and finite, whereas all terms with a higher-order k dependence diverge individually as $k\to\infty$. When treated in total these large-k divergent terms are convergent. The convergent low-order terms depend on the screening parameter according to $D^{2m-3}, D^{2m-5}, \ldots, D$, respectively. They therefore require a special treatment in the limit $D\to\infty$, i.e., the Coulomb limit. Instead of summing over higher-k terms at fixed m, the removal of these divergences requires a summation over all m at fixed s. The details and results of the few-body and many-body summations are given in Appendix B.

C. Quantum perturbation expansion of b_3

In Sec. II we were able to extend the known analytic results by means of a parametrized pseudopotential adjusted at each order so as to exactly reproduce rigorous results for the limit $\gamma_{ij}\to 0$. Only one of the parameters of the pseudopotential was allowed to be order dependent. The order-dependent parameter was found to change slowly with increasing order, suggesting that reliable results for high-order perturbation terms are obtained even when $\gamma_{ij}>1$. In the three-body case analytic results are not available and, furthermore, it is evident that in general each of the triad of two-particle connections should involve a different set of parameters. This is an attempt to account for the nonfactorizability of the singly connected quantum cluster coefficients[24] which enters at order $\hbar^4$.

A rigorous expression for the three-body ring term for Boltzmann particles is given by Eq. (17a). Since the one-component and many-component results are analytically similar only the one-component case is considered. A result similar to that for b_2^2 of Eq. (8a) is anticipated for the three-body ring diagram, but has proved to be analytically difficult. This is due to the fact that the following sum rule applies at second order[24]:

$$\sum_t L^2(X^2, 2\pi i t) = L(2X^2, 0) \tag{20}$$

whereas, at third order there is no similar result. Nevertheless, the first two terms have been obtained analytically, and very accurate evaluations of the following two terms have been determined from direct numerical calculation of Eq. (17a). The coefficients of the fifth to the seventh terms have also been determined within a few percent, and the result, valid for $\gamma' \equiv \gamma'_{ij} < 1$, is

$$b_3^r = (\beta\xi)^3\pi^2 D^2\left(\tfrac{1}{3} - \tfrac{1}{2}\gamma'^2 + 0.257\,479\gamma'^3 - 0.166\,667\gamma'^4 + 0.0842\gamma'^5 - 0.0346\gamma'^6 + 0.008\,66\gamma'^7\right). \tag{21}$$

The corresponding result obtained from the pseudopotential of Eq. (11) is

$$b_3^r = -(\beta\xi^2)^3\pi^2 D^3\{[1-(\gamma'/C)^3]/3 - 16(\gamma'/C)^2[\tfrac{1}{4}(1-\gamma'/C) - (\gamma'/C)/(1+\gamma'/C)]/[1-(\gamma'/C)^2]\}. \tag{22}$$

Following the procedure leading to Eqs. (12a)–(12f) and requiring Eq. (21) equal to Eq. (22) yields, for the leading coefficients in Eq. (12a),

$$h_{3,3} = 4, \quad a_{3,3,1} = -0.1503, \quad a_{3,3,2} = 0.0233. \tag{23}$$

Since $h_{3,3}$ is 18% larger than $h_{2,2}$ [Eq. (12c)] it appears that using a fixed value for C in Eq. (10) will not give the Coulomb ring sum very accurately. It turns out, however, that keeping C order independent introduces compensating errors. Figure 1 shows S_R/S_R^c vs γ_i from various calculations. The solid curve is the numerical evaluation of Eq. (17a) obtained by Graboske and DeWitt[25] the dashed curve is the much easier numerical evaluation of the ring sum using the pseudopotential of Eq. (10) with $C = h_{2,2} = 6/\sqrt{\pi}$, and the dotted curve is the small γ_i expansion of Sec. III B and Appendix C. The pseudopotential result is seen to be quite good and can be expected to give reliable results for higher-order many-body perturbation terms. If C is parametrized similar to Eq. (12a) even closer agreement can be obtained.

There is also a contribution at third order coming from the reducible, singly connected, diagram

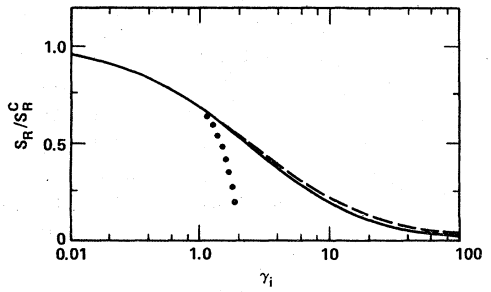

FIG. 1. Diffraction corrections to the ring sum. The solid curve is the numerical evaluation of Ref. 29, the dotted curve is the small γ expansion of Sec. III B, and the dashed curve was obtained with the pseudopotential of Eq. (10).

of Fig. 2. The contribution to b_3 from this diagram is given by

$$b_{3,\mathrm{rd}}^3 = 4 b_2^1 b_2^2 , \tag{24}$$

where b_2^1 and b_2^2 are given by Eq. (8b). The complete third-order term

$$b_3^3 = b_3^r + b_{3,\mathrm{rd}}^3 \tag{25}$$

involves three different functions $C(\gamma_i)$ reflecting the different ways that quantum effects enter at short distance. In an electrically neutral gas, required for stability in a plasma, all reducible terms involving b_2^1 cancel out.

Continuing on to higher-order terms, we note that those terms which diverge classically are of particular interest, since compensation between the bound- and scattering-state part of these terms will have an important effect on how composite particles are formed in an equilibrium plasma. For reasons already mentioned only the one-component case is considered. The diagrams that contribute at fourth-sixth order are shown in Fig. 3. These diagrams come from $b_2 - b_6$. Due to the large number of possibilities the reducible diagrams have only been included for b_3. Evaluation of the three-particle reducible diagrams for fourth–sixth order are given in Appendix D.

In the limit $D \to \infty$ the diagrams of Fig. 3 coming from b_2 all converge, but the diagrams coming from b_3 for $m \leq 6$ all diverge. When $m > 6$ the only

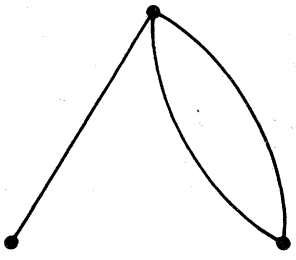

FIG. 2. Third-order reducible diagram.

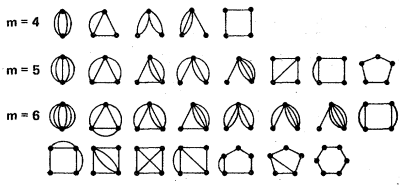

FIG. 3. Diagrams arising in the fourth through the sixth order in the coupling parameter. Only the three particle reducible diagrams are displayed.

irreducible diagrams in b_3 that diverge are the ones that have two lines coming in at one junction. Likewise, those reducible diagrams that have one, two, or three interaction lines joining two particles diverge. Mayer[26] and Abe[27] have shown that those irreducible diagrams in which at least three lines come in at each point are prototype diagrams, which when summed over similar diagrams occurring in higher b_n, replace D with λ_D in the Coulomb limit, e.g., the irreducible diagram for $m=4$ is a member of the infinite set of diagrams shown in Fig. 4, which screens one rung of the three rung ladder diagram (indicated by wavy line). The reducible diagrams may be screened in a similar way. For b_3 all those reducible diagrams that are not removed by electrical neutrality are necessarily prototype diagrams. A generating procedure for screening the reducible diagrams was given in I. As a result of screening, the virial and cluster coefficients for a Coulomb gas are replaced with the corresponding result for the Debye potential, but with all those diagrams which are not prototypes subtracted out. The above statements are only valid when $\gamma \ll 1$, otherwise, the many-body potential takes a very complicated form.[28] If for simplicity, and in view of Fig. 1, it is assumed that the parameters $C_{n,m}$ in our order-dependent pseudopotential are all the same, the resultant screened potential becomes[29,30]

$$U_{\mathrm{eff}}^S = (\xi_i \xi_j / \epsilon r)(e^{-\alpha_- r} - e^{-\alpha_+ r}) , \tag{26a}$$

$$\alpha_\pm = (C/\sqrt{2}\lambda_{ij})(1 \pm \epsilon)^{1/2}, \quad \epsilon = (1 - 4\gamma_{ij}^2/C^2)^{1/2} ,$$

$$\gamma_{ij} = \lambda_{ij}/\lambda_D . \tag{26b}$$

This is analytically of the same form as Eq. (11), so that the many-body result can be obtained from the few-body perturbation terms by simply replacing $1/D \to \alpha_-$, $C \to \alpha_+ \lambda_{ij}$ and multiplying by the appropriate power of $1/\epsilon$. Further refinement can be obtained by considering the order dependence of the $C_{n,m}$. The fact that terms involving square

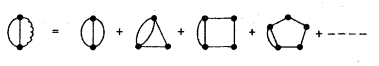

FIG. 4. Set of diagrams that screen one rung of the three rung ladder (or watermelon) diagram.

roots arise in Eq. (26) is of no importance to the few-body compensation since it results from cancellations in terms involving fractional powers of the potential, prior to forming the many-body sum.

In order to use the results of this section in a cluster expansion it is necessary to find generalized forms of Eqs. (13) and (14a). Each n-body cluster term involving j electrons must be separated into j parts[2] having activity dependence of order $n-j$. The diagrams of Fig. 3 can be associated with the proper bound electron-ion clusters by counting the number of electron-ion connections that have an even number of interaction lines.

IV. DISCUSSION

The different analytical behavior of the bound- and scattering-state parts of the trace, for kT less than the binding energy, requires a renormalization of the activity series. Tightly bound clusters clearly act like new particles, whereas, similar clusters in highly excited states may more closely resemble two-particle scattering events. Treating these weakly bound clusters as particles can lead to gross errors in the ideal gas limit. It was shown in this paper that the analytic properties of the trace leads to a natural separation into effective bound- and scattering-state parts. This results from a compensation of all those terms in the few-particle bound-state sum, which have a large orbit divergence, with scattering-state terms. Quantum effects prevent complete compensation of the deepest bound states. This will effect the quantitative details and requires additional investigation. It remains to be shown that the analytic properties produce a universal definition for composite particle activities applicable even to high-order scattering events involving one or more of the tightly bound clusters.

We have also greatly extended the known quantum perturbation results; both for the few-body problem and the closely related many-body problem. The analysis involved a combination of rigorous quantum statistical mechanics, semiclassical theory, and pseudopotential methods. The results are qualitatively correct and there is reason to expect that there are no gross errors in the quantitative details. In the future we anticipate using extended versions of the present work to evaluate high-order terms in the Coulomb activity expansion developed in II.

ACKNOWLEDGMENT

The author would like to thank H. E. DeWitt for encouragement and many stimulating discussions during the course of the work. Thanks is also extended to H. C. Graboske for providing his calculations of the quantum ring sum. This work was performed under the auspices of the U. S. Department of Energy by the Lawrence Livermore Laboratory under Contract No. W-7405-ENG-48.

APPENDIX A: PERTURBATION EXPANSION OF THE SECOND COEFFICIENT

The perturbation terms for the potential of Eq. (11) can be obtained analytically in all orders, but become unwieldy for high order.[31] The three and four rung ladder terms are given by

$$b_{ij}^{m} = 2\pi(-\beta)^{m}\phi_{m}(D, \lambda_{ij}/C)/m! \,, \tag{A1}$$

where

$$\phi_{m}(D, \lambda_{ij}/C) = \int_{0}^{\infty} dr\, r^{2} U_{\mathrm{eff}}^{m}(r, D, \lambda_{ij}/C) \,, \tag{A2}$$

$$\phi_{3} = (\xi_{i}\xi_{j})^{3}\left[\ln\gamma_{c} + 3\ln\left(\frac{2+\gamma_{c}}{1+2\gamma_{c}}\right)\right] , \tag{A3}$$

$$\phi_{4} = (\xi_{i}\xi_{j})^{4}\,\frac{C}{\lambda_{ij}}\left\{\ln\left(\frac{2^{20}}{3^{12}e^{4}}\right) + 4\gamma_{c}\left[\ln\gamma_{c} + \ln\left(\frac{32}{3e}\right) - \left(1+\frac{3}{\gamma_{c}}\right)\ln\left(\frac{1+\gamma_{c}/3}{e}\right) + 3\left(1+\frac{1}{\gamma_{c}}\right)\ln\left(\frac{1+\gamma_{c}}{e}\right) - 3\left(1+\frac{\gamma_{c}}{3}\right)\ln\left(\frac{1+3\gamma_{c}}{e}\right)\right]\right\} , \tag{A4}$$

and $\gamma_{c} = \gamma'_{ij}/C$. The leading terms for ϕ_{5} and ϕ_{6} when $\gamma'_{ij} < 1$ are given by

$$\phi_{5} = (\xi_{i}\xi_{j})^{5}\left(\frac{C}{\lambda_{ij}}\right)^{2}[0.240\,808\,8 - 3.398\,01\gamma_{c} - 12.5\gamma_{c}^{2}(\ln\gamma_{c} + 1.1235)] \,, \tag{A5}$$

$$\phi_{6} = (\xi_{i}\xi_{j})^{6}\left(\frac{C}{\lambda_{ij}}\right)^{3}[0.118\,537\,2 - 1.444\,85\gamma_{c} + 11.9448\gamma_{c}^{2} - 36\gamma_{c}^{3}(\ln\gamma_{c} - 1.016\,67)] \,. \tag{A6}$$

Equations (A1)–(A6) are sufficient to see the structure of high-order terms. The terms left out of Eqs. (A5) and (A6) are similar to the logarithmic terms of Eqs. (A3) and (A4). In the limit $\gamma'_{ij} \to \infty$, $\gamma_{c} \to 1$ and each $\phi_{n} \to 0$. The sum over all ϕ_{n} for a fixed γ'_{ij} is nevertheless finite.

In the limit $\gamma'_{ij} \to 0$

$$\phi_{3} = \ln\gamma'_{ij} + D'_{a} \,, \tag{A7}$$

where

$$D_q' = \ln(8/h_{2,3}) = \ln(\tfrac{4}{3}\pi^{1/2}) = 0.8600\,, \tag{A8}$$

when $h_{2,3} \equiv h_{2,2}$. The pseudopotential Eq. (11) reproduces the limiting results of Eq. (A7) very well, i.e., the logarithmic term is exactly the same and $D_g' = 0.969\ D_g$ [see Eq. (8d)]. Solving for the value of $h_{2,3}$ that satisfies $D_q' = D_q$ gives

$$h_{2,3} = 0.973 h_{2,2}\,. \tag{A9}$$

The very small adjustment needed in the dominant parameter $h_{2,2}$ suggests that even smaller changes in the $a_{2,2,\nu}$ are required to exactly reproduce the third-order term for all γ_{ij}', i.e., Eq. (A1) using Eqs. (A4), (12d)–(12f), and (A9) is a very good approximation to b_{ij}^3 for all γ_{ij}'. Comparison of Eqs. (A4)–(A6) with the small γ_{ij}' limit results of Ebeling, Eqs. (9a) and (9b), gives

$$\frac{\phi_4}{\phi_{E,4}} = \frac{4\Gamma(3)}{\pi^{5/2}} h_{2,4} \ln(2^{20}/3^{12}) = 1 \tag{A10}$$

when $h_{2,4} = 0.951 h_{2,2}$;

$$\frac{\phi_5}{\phi_{E,5}} = \frac{0.2408(2)^5\Gamma(7/2)}{\sqrt{\pi}\,\zeta(3)5!}\, h_{2,5}^2 = 1 \tag{A11}$$

when $h_{2,5} = 0.933 h_{2,2}$;

$$\frac{\phi_6}{\phi_{E,6}} = \frac{0.1185(2)^6\Gamma(4)}{\sqrt{\pi}\,\zeta(4)6!}\, h_{2,6}^3 = 1 \tag{A12}$$

when $h_{2,6} = 0.921 h_{2,2}$. Equations (A10)–(A12) show that the adjustment to $h_{2,2}$ required to exactly recover the $\gamma_{ij}' \to 0$ limit increases but at a decreasing rate as m increases, i.e., the pseudopotential of Eq. (11) should give a good approximation to the first few b_{ij}^m for all γ_{ij}' when the $C_{2,m}$ as defined by Eqs. (12d)–(12f) and Eqs. (A10)–(A12). A useful extension of Eqs. (8b) and (9a) to finite values of γ_{ij}' has, therefore, been obtained.

APPENDIX B: SEMICLASSICAL TWO-ELECTRON BOUND-STATE PARTITION FUNCTIONS

The three-body bound-state problem is complicated even in the semiclassical approximation, so that additional approximation is made. We first assume no lifting of the m degeneracy, so that the bound-state part of $b_{ee\alpha}$ becomes

$$\begin{aligned}\frac{b_{ee\alpha}^b}{16\pi^3 \lambda_{e\alpha}\lambda_{eH}} \equiv Q_{ee\alpha} &= \sum_i g_i \exp(-\beta E_i) \\ &\simeq \sum_{n_1 l_1} (2l_1+1)\exp(-\beta E_{n_1 l_1}) \\ &\quad \times \sum_{n_2 l_2 \geq n_1 l_1} (2l_2+1) \\ &\quad\quad \times \exp(-\beta E_{n_1 l_1 n_2 l_2})\,,\end{aligned} \tag{B1}$$

where i is any good set of quantum numbers $E_{n_1 l_1 n_2 l_2}$ is the energy of state $n_1 l_1 n_2 l_2$ relative to state $n_1 l_1$ and H signifies a one-electron composite of mass $m_H = m_e + m_\alpha$. It was shown in the Appendix of II that, when $(n_1 l_1) = (1,0)$, the states $E_{10 n_2 l_2}$ can be calculated, within a few percent, from the potential

$$V_{nl}(r) = -\frac{e^2}{r}[(Z-1)\exp(-r/D) + \exp(-Z\epsilon_{nl} r)]\,, \tag{B2}$$

where

$$\epsilon_{10} = 1.067 + 0.087/(ZD/a_{e\alpha})^2\,. \tag{B3}$$

As ZD decreases the energy levels are weakened until at $D = D_c = 0.840\ a_{e\alpha}/Z$ they have all moved into the continuum. At $D = D_c$ the core electron screening is totally ineffective and $Z\epsilon_{nl}(ZD/a_{e\alpha}) \to 1/D$. For doubly excited states it is assumed that ϵ_{nl} scales with the radius $(D \to \infty)$ s_{nl} of the innermost occupied state, i.e.,

$$\epsilon_{nl} = a_{e\alpha}\epsilon_{10}/Z\langle s_{nl}\rangle\,. \tag{B4}$$

When $(n_1 l_1) = (1,0)$ the sum over the bound and scattering states of the outermost electron can be replaced with WKB expressions exactly as in the two-body case. The compensation is, therefore, essentially the same except there will be some modification at short distance due to uncertainty and Pauli principle effects. In general, however, both electrons can occupy high orbits and the divergence is now much worse than in the two-body case. The analysis of these states will be based on the fact that the divergence of the Boltzmann sum is essentially classical, such that, diffraction and quantum statistical effects only enter the quantitative detail.

For doubly excited states the sum over $(n_2 l_2)$, by definition, excludes some of the low-lying states. The semiclassical integration over these states now starts, approximately, at the radius of the highest-lying excluded state. If the sum over $(n_1 l_1)$ is also replaced by an integral the following generalization of the one-electron semiclassical bound-state partition function[6] is obtained (in a.u.)

$$\begin{aligned}Q_{ee\alpha} = \frac{1}{\pi^2}\int_0^\infty d\tau\, \tau^2 e^{-g(\tau)} &\times \int_0^{-V(\tau)} du\,\sqrt{u}\, e^{-u/T_Z} \\ &\times \int_\tau^\infty d\rho\,\rho^2 e^{-g'(\tau,\rho)} \\ &\times \int_0^{-V'(\tau,\rho)} dw\,\sqrt{w}\, e^{-w/T_Z}\,,\end{aligned} \tag{B5}$$

where

$$V(\tau) = -2e^{-\tau/d}/\tau\,, \tag{B6}$$

$$V'(\tau,\rho) = -2\{(Z-1)e^{-\rho/d} - \exp[-a_{e\alpha}\epsilon(\tau)\rho]\}/Z\rho\,, \tag{B7}$$

$$g = -V/T_Z,\quad g' = -V'/T_Z,\quad T_Z = kT/R_Z\,, \tag{B8}$$

$$\rho = Zr/a_{e\alpha}, \quad \tau = Zs/a_{e\alpha}. \tag{B9}$$

The generalization of Eq. (17a) to multielectron terms is apparent. The quantitative accuracy of these calculations is doubtful, but they should give the correct analytic forms and that is sufficient for the present arguments.

APPENDIX C: DIFFRACTION AND DEGENERACY CORRECTIONS TO THE DEBYE-HÜCKEL TERM

Working first with the many-body part of the ring diagrams, described in Sec. III B, and summing sequentially the most divergent terms from each b_n, the next most divergent terms, etc., gives

$$S_{R,\mathrm{mb}} = \sum_{n=2}^{\infty} z^n b^r_{n,mb} = \frac{4\pi z}{2(2\pi)^3} \int_0^{\infty} dk\, k^2 \left[\sum_{n=2}^{\infty} \frac{w_n}{n} + \sum_{\nu=3}^{\infty} (k^2\gamma_i^2)^{\nu-2} \sum_{n=\nu}^{\infty} \sum_{\mu=1}^{\nu-2} \left(\prod_{j=0}^{\mu-1} (n-j) \right) \frac{H_{\nu,\mu} w^n}{n} \right] \tag{C1}$$

where

$$\gamma_i = \lambda_i/\lambda_D, \quad \lambda_D = (4\pi\beta\xi^2 z)^{1/2}, \tag{C2}$$

z is the activity defined by Eq. (4),

$$w = -1/[\lambda_D^2(k^2 + 1/D^2)], \tag{C3}$$

$$\sum_{\mu=1}^{\nu-2} H_{\nu,\mu} \tag{C4}$$

is the coefficient of the term $(\gamma_i^2 k^2)$ in the expansion of $\exp[(L(X^2, 0) - 1)]$, μ is the order of the factor $(L(X^2, 0) - 1)^{\mu}$ producing the $H_{\nu,\mu}$ component of the coefficient, e.g., $H_{3,1} = a_1$, $H_{4,1} = a_2$, $H_{4,2} = \frac{1}{2}a_1^2$, and the a_s are given by Eq. (18).

Each sum in Eq. (C1) can be generated from derivatives of the function

$$Y_{\nu} = \int \frac{dw\, w^{\nu-1}}{1-w} \tag{C5}$$

according to

$$S_{R,\mathrm{mb}} = S_R^c \left(f + \frac{3}{2} \sum_{\nu=3}^{\infty} A_{\nu-1} \gamma_i^{2\nu-4} \right), \tag{C6}$$

where

$$S_R^c = 1/12\pi\lambda_D^3 \tag{C7}$$

is the Debye-Hückel classical limit,

$$f = (1+\epsilon_D)^{3/2} - \tfrac{3}{2}\epsilon_D - \epsilon_D^3, \quad \epsilon_D = \lambda_D/D, \tag{C8}$$

$$A_{\nu-1} = \sum_{\mu=1}^{\nu-2} H_{\nu,\mu} \theta_{\nu,\mu}, \tag{C9}$$

and

$$\theta_{\nu,\mu} = \frac{2}{\pi} (-1)^{\nu} \lambda_D^{2\nu-1} \int_0^{\infty} dk\, k^{2\nu-2} w^{\nu-2} \frac{d^{\mu} Y_{\nu}}{dw^{\mu}}. \tag{C10}$$

In the Coulomb limit ($D \to \infty$) the first few $\theta_{\nu,\mu}$ are

$$\theta_{\nu,1} = 1, \quad \theta_{\nu,2} = \nu - \tfrac{3}{2}; \tag{C11}$$

$$\theta_{\nu,3} = (\nu-2)^2 - \tfrac{1}{4}, \quad \theta_{\nu,4} = (\nu-3)^3 - \tfrac{19}{4}\nu - \tfrac{57}{8}; \tag{C12}$$

so that

$$A_2 = a_1\theta_{3,1} = \tfrac{1}{6}, \quad A = a_2\theta_{4,1} + \tfrac{1}{2}a_1^2\theta_{4,2} = \tfrac{37}{720}; \tag{C13}$$

$$A_4 = a_3\theta_{5,1} + a_1a_2\theta_{5,2} + a_1^3\theta_{5,3}/3! = \tfrac{641}{36288}. \tag{C14}$$

To compare with the results of DeWitt[23] we need to expand his Eq. (44) in powers of γ_i^2. This gives exact agreement with A_2 and A_3 but his a_4 is incorrectly evaluated.[32] The correct value is $a_4 = 0.141\,534$.

The few-body part of the ring sum is given by

$$S_{R,\mathrm{fb}} = \frac{3}{\pi} S_R^c \sum_{n=2}^{\infty} A'_n \gamma_i^{2n-3}, \tag{C15}$$

where

$$A'_n = \frac{1}{n\gamma_i^{2n-3}} \int_0^{\infty} \frac{dk\, k^2}{(k^2 + 1/D^2)^n} \left(\sum_{t=-\infty}^{t=+\infty} L^n(X^2, 2\pi i t) - \sum_{s=1}^{n-2} (\gamma_i^2 k^2)^{s-1} G_s \right) \tag{C16}$$

and

$$G_1 = n, \quad G_2 = na_1, \quad G_3 = n[a_2 + (n-1)a_1^2/2], \text{ etc.}, \tag{C17}$$

are the parts of L already used in the many-body problem. Numerical evaluation of some of the A'_n gives

$$A'_2 = 0.492\,175, \quad A'_3 = 0.142\,845, \quad A'_4 = 0.046\,525, \quad A'_5 = 0.016\,71. \tag{C18}$$

The A'_n are numerically identical to the corresponding coefficients given by Eq. (43) of DeWitt.[33] We note that the two-body component of Eq. (C17) is of the form $\lambda^3 E/kT$ indicating that terms of this type, as already mentioned, are not completely compensated in the two-body trace.

The results given for the ring terms are rigorous for nonrelativistic Boltzmann particles, provided $\gamma_i < 1.43$, since the power series does not converge for larger γ_i. It may be, however, that the radius of convergence of the power series expansion is increased when similar terms coming from nonring diagrams are included. For fermions and bosons the $L(X^2, 2\pi i t)$ function is modified by degeneracy and exchange effects. Inclusion of degeneracy gives[34]

$$\mathfrak{L}(X_i^2, 2\pi i t) = L(X_i^2\mathfrak{D}, 2\pi i k\mathfrak{D})\mathfrak{F}_{-1/2}(\alpha_i)/\xi\,, \qquad \text{(C19)}$$

where $\mathfrak{D}$ is the operator $d/d\alpha_i$, $\mathfrak{F}_{-1/2}(\alpha_i)$ is a Fermi or Bose integral, $\alpha_i = \mu_i/kT$, $\xi = \mathfrak{F}_{-1/2}(\alpha_{0i})$, and α_{0i} is μ/kT for the noninteracting system. For $t = 0$ this gives

$$\mathfrak{L}(X_i^2, 0) = \xi^{-1}\sum_{s=0}^{\infty} a_s\,\mathfrak{F}_{-(2s+1)}(\alpha_i)X_i^{2s}\,. \qquad \text{(C20)}$$

Since the effect on a given type of term is the same for all n, the A_{v-1} become

$$A_2 = a_1\xi^{-1}\mathfrak{F}_{-1/2}\,, \qquad \text{(C21)}$$

$$A_3 = a_3\xi^{-1}\mathfrak{F}_{-3/2}\theta_{4,1} + \tfrac{1}{2}(a_1\xi^{-1}\mathfrak{F}_{-1/2})^2\theta_{4,2}, \quad \text{etc.} \qquad \text{(C22)}$$

Due to the fact that each term in the k expansion involves a different $\mathfrak{F}$ function, no simple result similar to that for the A_{v-1} emerges. Degeneracy corrections to the A_n' can, nevertheless, be developed by expanding the $\mathfrak{F}_n$.

APPENDIX D: HIGH-ORDER PERTURBATION TERMS FOR b_3

In transform space the irreducible part of b_3 is given by

$$b_{3,\mathrm{ir}} = -\frac{B_3}{2} = \frac{-1}{12\pi^2}\int_0^\infty dk\,k^2\tilde{f}^3(k) \qquad \text{(D1)}$$

where

$$\tilde{f}(k) = \int_0^\infty d\vec{r}\,f(r)e^{i\vec{k}\cdot\vec{r}}\,, \qquad \text{(D2)}$$

and

$$f(r) = e^{-\beta U_{\mathrm{eff}}} - 1\,. \qquad \text{(D3)}$$

Expansion of $f(k)$ in powers of the potential gives

$$f(k) = \sum_i \tilde{f}_i\,, \qquad \text{(D4)}$$

where the first few $\tilde{f}_i$ are given by

$$\tilde{f}_1 = -(4\pi\beta\xi^2)\left[\frac{1}{k^2+1/D^2} - \frac{1}{k^2+a^2}\right], \quad a = \frac{C}{\lambda_{ii}} \qquad \text{(D5)}$$

$$\tilde{f}_2 = \frac{4\pi(\beta\xi^2)^2}{2!k}\left(\tan^{-1}\frac{kD}{2} - 2\tan^{-1}\frac{kD}{1+aD} + \tan^{-1}\frac{k}{2a}\right) \qquad \text{(D6)}$$

$$\tilde{f}_3 = -\frac{4\pi(\beta\xi^2)^3}{3!k}\left[\frac{k}{2}\ln\left(\frac{3a^2+k^2}{3/D^2+k^2}\right) + \frac{3k}{2}\ln\left(\frac{(1/D+2a)^2+k^2}{(2/D+a)^2+k^2}\right) + 3a\tan^{-1}\frac{k}{3a} - \frac{3}{D}\tan^{-1}\frac{kD}{3} + 3\left(\frac{2}{D+a}\right)\tan^{-1}\frac{kD}{2+aD} - 3\left(\frac{1}{D+2a}\right)\tan^{-1}\frac{kD}{1+2aD}\right], \qquad \text{(D7)}$$

$$\tilde{f}_4 = \frac{4\pi(\beta\xi^2)^4}{4!}\,\tfrac{2}{3}e^{-5ka/4}\,. \qquad \text{(D8)}$$

Due to the length of the $\tilde{f}_4$ term it has been replaced by an approximate form which is asymtotically correct as $k \to 0$.

Since the reducible diagrams in Fig. 3 factor into $4(b_2)^2$ they can be readily evaluated with the results of Sec. II. The irreducible diagram for $m = 4$ is given by

$$b_{3,\mathrm{ir}}^4 = -B_3^4/2 = \frac{-3(\beta\xi^2)}{12\pi^2}\int_0^\infty dk\,k^2\tilde{f}_1^2\tilde{f}_2\,. \qquad \text{(D9)}$$

In its most general form Eq. (D9) involves two different functions $C(\gamma')$ where $C = g_1(\gamma')$ is appropriate for $\tilde{f}_1$, and $C = g_2(\gamma')$ is appropriate for $\tilde{f}_2$. The best available estimate for g_1 and g_2 are $g_1 = C_{3,3}$ and $g_2 = C_{22}$. After an integration over r in $\tilde{f}_1$ Eq. (D9) becomes

$$b_{3,\mathrm{ir}}^4 = 4\pi^2(\beta\xi^2)^4\int_0^\infty dk\,dr\,kr\sin kr \times\left(\frac{1}{k^2+1/D^2} - \frac{1}{k^2+g_1^2/\lambda_{ii}}\right)^2 U_{\mathrm{eff}}^2(r, \lambda_{ii}/g_2^2)\,. \qquad \text{(D10)}$$

Integration of Eq. (D10) over k gives a result which can be written in the form

$$b_{3,\mathrm{ir}}^4 = -4\pi^2\beta\xi^2\left(D^3\frac{\partial\phi_3}{\partial D} + \frac{4\Phi_3}{1/D^2 - g_1^2/\lambda_{ii}} + \frac{\lambda_{ii}^2}{g_1}\frac{\partial\Phi_3}{\partial g_1}\right), \qquad \text{(D11)}$$

where

$$\Phi_3 = (\beta\xi^2)^3\left[\ln\left(\frac{3}{D(2g_1+g_2)}\right) - 2\ln\left(\frac{2/D+g_2}{1/D+g_1+g_2}\right) - \ln\left(\frac{2/D+g_1}{1/D+2g_2}\right)\right],$$

when $g_1 = g_2$, $\Phi_3 = \phi_3$, where ϕ_3 is given by Eq. (A3).

The surviving reducible diagram for $m = 4$ is given by $b_{3,\mathrm{rd}}^4 = 2(b_2^2)^2$, where b_2^2 is given by Eq. (8b). The many-body sum over the reducible diagrams, involving two rings connected at one junction also replaces D with λ_D as $D \to \infty$. This replacement comes about in a somewhat different way than for the reducible diagrams. As shown in I the sum over these diagrams is given by the following operation on S_R:

$$\frac{z}{2}\left(\frac{\partial S_R}{\partial z}\right)^2, \tag{D12}$$

where S_R depends on the activity through Eq. (3).

For $m=5$ the irreducible part of b_3^5 has two topologically distinct parts, as shown in Fig. 3. The prototype diagram will be labeled b_{3a} and the other diagram will be labeled b_{3b}. Since b_{3b}^5 is topologically similar to $b_{3,\mathrm{ir}}^4$ it can be evaluated in the same way, with a result similar to Eq. (D11), except $\phi_3 \to \phi_4$ and $\Phi_3 \to \Phi_4$. It is not displayed here, but Φ_4 is a two parameter form of ϕ_4 which is given by Eq. (A4). The prototype part of b_3^5 is given by

$$b_{3,a}^5 = -B_{3,a}^5/2 = \frac{-3}{12\pi^2}\int_0^\infty dk\, k^2 \tilde{f}_1 \tilde{f}_2^2$$
$$= -8\pi(\beta e^2)^5[F(D) - F(1/C)], \tag{D13}$$

where

$$F(a) = I(D,D,a) - 4I(D,E,a) + 2I(D,1/C,a) + I(E,E,a) - 4I(E,1/C,a) + I(1/C,1/C,a), \tag{D14}$$

$$E = 2/(1/D + C), \tag{D15}$$

and

$$I(\mu,\nu,\omega) = \int_0^\infty \frac{dk \tan^{-1}(k\mu/2)\tan^{-1}(k\nu/2)}{k^2 + 1/\omega^2}. \tag{D16}$$

A complete analytic result for $I(\mu,\nu,\omega)$ has not been obtained. The main terms for small γ' are given by the following semianalytic result:

$$I(\mu,\nu,\omega) = \tfrac{1}{4}\pi\mu \ln[(\nu/\mu)(1.792\,154 + \mu/\nu + 0.020\,035 e^{-4.687\,09\mu/\nu})]. \tag{D17}$$

Equation (D17) is accurate everywhere to three significant figures and to six significant figures when $\mu/\nu \gg 1$, $\ll 1$, or 1. Also when $\omega \gg (\mu,\nu)$

$$I(\mu,\nu,\omega) = \tfrac{1}{2}\pi \ln[(\mu+\nu)^{\mu+\nu}/\mu^\mu \nu^\nu]. \tag{D18}$$

The many-body sum over the diagrams that screen the surviving reducible terms, again using the method of I gives

$$z\frac{\partial}{\partial z} z\left(\frac{\partial S_R}{\partial z}\right)\left[\frac{\partial z^3 b_2^3(\lambda_D)}{\partial z}\right], \tag{D19}$$

where $b_2^3(\lambda_D)$ is approximated by Eqs. (A1) and (A3) and the many-body substitutions for the potential of Eq. (30a) described earlier.

At sixth order there will be contributions from prototype diagrams in b_2, b_3, and b_4 whose complete analysis is too lengthy to be attempted in this paper. For the present the analytic form of the irreducible diagrams in b_3 at sixth order is sufficient. Labeling the symmetric prototype diagram as $b_{3,a}^6$ and the unsymmetric prototype diagram $b_{3,b}^6$ and the remaining diagram $b_{3,c}^6$ it is found semianalytically that, for $\gamma' < 1$,

$$b_{3,a}^6 \equiv -B_{3,a}^6/2 = -(\beta\xi^2)^6\left[\frac{2\pi^3}{3}\left(\frac{\pi}{8} + 2.793\,66\,\frac{\gamma'}{C_{2,2}}\right)\ln\left(\frac{\gamma'}{C_{2,2}}\right) - 1.454\,887\right], \tag{D20}$$

$$b_{3,b}^6 \equiv -B_{3,b}^6/2 = -(\beta\xi^2)^6\left(\frac{4\pi^2}{3}\left\{\frac{\pi}{4}\left[\ln^2\left(\frac{\gamma'}{c_b}\right)\right]^2 - 1.6958\ln\left(\frac{\gamma'}{c_b}\right) - 2.3592\right\}\right), \tag{D21}$$

$$b_{3,c}^6 \equiv -B_{3,c}^6/2 = -(\beta\xi^2)^6 \tfrac{16}{45} C_c/\gamma', \tag{D22}$$

where for simplicity, the averages

$$C_b = (C_{3,3}C_{2,2}C_{2,3})^{1/3}, \quad C_c = (C_{3,3}^2 C_{2,4})^{1/3} \tag{D23}$$

have been used. The only divergences in the higher-order terms of b_3 occur for diagrams of the type $b_{3,c}$ which diverge $\propto 1/\lambda_{ij}^{n_{ij}}\gamma'$.

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