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Statistical mechanics of Coulomb gases of arbitrary charge*

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The Coulomb-gas activity expansion of Rogers and DeWitt is extended to include more terms. This is an expansion in the activities of electrons and nuclei, and it converges slowly in regions where composite particles are present. It is shown that by treating certain products of terms as composite-particle activities, the convergence of the expansion is greatly increased. The important element of the present work is the recognition that terms in the original expansion correspond to the Taylor-series expansions of a similar expansion involving an augmented set of activity variables, i.e., the composite particles enter the expansion similar to fundamental particles (electrons and nuclei). This reorganization of the activity expansion makes it possible to calculate the equation of state for electron-nucleus gases of any charge. All stages of ionization and dissociation are treated to the same order of approximation in the new expansion. To illustrate these features some calculations for helium are given. To demonstrate the improved convergence properties, some calculations for hydrogen are compared with those obtained by Rogers and DeWitt.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as I, it was demonstrated that the cluster (activity) expansion is the natural expansion to use for reacting gases. However, for Coulomb gases, as is well known, each of the cluster coefficients b_n diverges in the limit $V \to \infty$ so that the formation of binary, trinary, etc., composite particles cannot be handled in a simple way. This problem was dealt with in I, where it was shown how to expand the b_n in powers of the potential and collect the resultant terms such that all long-range divergences are eliminated.[2] The activity expansion thus obtained was reordered into an expansion resembling the cluster expansion for an ordinary gas. A shortcoming of this latter expansion is that it converges slowly in regions where composite particles are formed. The purpose of this paper will be to demonstrate that the activity expansion given in I, which only involves the activities of electrons and nuclei, can be rewritten in terms of an augmented set of activity variables with improved convergence properties. The formation of composite particles, described in terms of the activities of fundamental particles, is associated with exponentially increasing Boltzmann factors $e^{|E|/kT}$ at low temperatures. This exponential increase with decreasing temperature forces the activities, through the density constraints, to decrease such that the product of the activities and $e^{|E|/kT}$ is of the size of the density of composite particles. This product of terms acts as though it is of unit power in the activity. As a result, terms involving the product enter the expansion effectively as the power of the product rather than the power of the activities. In the new expansion these product terms are considered to be the activities of composite particles. The utility of the new expansion is that, by explicitly identifying quantities that act like composite-particle activities, one automatically includes the Coulomb effects in the original expansion that are important at any stage of ionization.

The formal development will be rigorous in the limit that the ratio of the de Broglie wavelength (λ) to the Debye length (λ_D) approaches zero. This comes about as follows: The logarithm of the grand partition function,

$$\ln Z_{\text{gr}} = \ln \operatorname{Tr} e^{-\alpha N - \beta H},$$

is expanded, for Boltzmann particles, using diagrammatic perturbation techniques similar to those used in field theory. As discussed in I, this results in expressions which resemble the cluster coefficients of the dynamic screened Coulomb potential, except because of the summation procedure which eliminated the Coulomb divergencies, certain types of terms are subtracted out. In addition new types of terms are present which are related directly to the presence of the plasma. The terms that resemble cluster coefficients involve two distinct quantum diffraction parameters $\eta = \lambda/\beta e^2$ and $\gamma = \lambda/\lambda_D$, but the purely plasma terms only involve γ. In the limit $\gamma \to 0$, therefore, there is a well-defined region for which the many-body plasma part of the problem remains classical while the few-body part displays the necessary uncertainty-principle effects at short distances. In this limit the dynamic screened Coulomb potential goes over to the Debye potential (see Appendix B of I) and all the propagators except those associated with $e^{-\beta H}$ are classical. This limit is equivalent to replacing the Boltzmann factors of the classical theory, minus their appropriately subtracted parts, with a Slater sum. As a result of the simplicity afforded by this correspondence, we perform our preliminary analysis classically but ultimately insert Slater sums at the proper places.

For two-body interactions it is far easier to evaluate r-space integrals over the Slater sum, i.e.,

$$\mathrm{Tr}(e^{-\beta H_2}-e^{-\beta H_0}),$$

using the Beth-Uhlenbeck procedure[3] rather than the perturbation expansion. For three- or more-body terms there is no easy way to evaluate the trace. However, the most important part of the trace at low to moderate density, i.e., those states for which at least $n-1$ of the n particles of the cluster are bound, can be obtained relatively easily. This is done by first performing an accurate variational calculation of a few of the lowest states and from this determining an effective two-body potential. Next the Beth-Uhlenbeck procedure is used to perform the trace over single-particle excited states. The states that are ignored correspond to processes in which three or more fundamental or composite particles enter into a single scattering event. This clearly limits our calculations to low and moderate densities, consistent with the already stated assumption that $\gamma \to 0$. Nonetheless, the results are useful since they yield an unambiguous Saha result as the density goes to zero and also include classical plasma corrections, even in the presence of composite particles. Since the z^3 terms require an explicit consideration of three-body scattering states, the analysis is carried only through $z^{5/2}$ terms in the activity.

II. ONE-COMPONENT GAS

Reorganization of the activity expansion for a gas of electrons and nuclei, as mentioned above, requires extensive analysis. For this reason it will be useful to first illustrate the main features with the simplest possible example, i.e., the one-component gas. In this section we first consider an ordinary reacting gas having only one basic component, e.g., hydrogen atoms, and show why it is useful to introduce a new activity variable for each possible bound state. Second, we consider a hypothetical one-component Coulomb gas that can have bound states, and show that the plasma interactions arising from the composite particles must be treated on an equal basis with those arising from the fundamental particles.

A. Ordinary gas

Because of their utility in the Coulomb problem, we begin the discussion with the introduction of the S and C expansions.

In I it was shown that the activity expansion can be expressed according to

$$\frac{P}{kT}=z+S+\sum_{m=2}^{\infty}\frac{z}{m!}\left(\frac{\partial}{\partial z}\right)^{m-2}\left(\frac{\partial S}{\partial z}\right)^{m}, \tag{1}$$

where the differential operator acts $m-2$ times on $(\partial S/\partial z)^m$, the classical expression for S is

$$S(z)=\sum_{J=2}^{\infty}\frac{z^J\beta_{J-1}}{J}, \tag{2}$$

the β_{J-1} are Mayer cluster integrals,

$$z=(2s+1)\lambda^{-3}e^{\mu/kT}$$

is the activity,

$$\lambda=(2\pi\hbar^2/mkT)^{1/2}$$

is the de Broglie wavelength, s is the spin, and μ is the chemical potential. The activity is eliminated from Eq. (1) by means of the density equation

$$\mathfrak{N}=z\frac{\partial(P/kT)}{\partial z}.$$

Equation (1) is transformed to a cluster expansion by grouping together all terms of the same power in z, with the result

$$\frac{P}{kT}=z+\sum_{n=2}^{\infty}C_n, \tag{3}$$

where

$$C_2=Y_2, \tag{4}$$

$$C_3=Y_3+\frac{z}{2}\left(\frac{\partial Y_2}{\partial z}\right)^2, \tag{5}$$

$$C_4=Y_4+z\frac{\partial Y_2}{\partial z}\frac{\partial Y_3}{\partial z}+\frac{z}{3!}\frac{\partial}{\partial z}z\left(\frac{\partial Y_2}{\partial z}\right)^3, \tag{6}$$

etc., and, in the classical case,

$$Y_J\equiv\beta_{J-1}z^J/J. \tag{7}$$

In the quantum-mechanical problem the cluster integrals are replaced with the appropriate traces over exponential Hamiltonian operators. The C_n are related to the cluster coefficients b_n according to

$$C_n/z^n=b_n. \tag{8}$$

Equation (3) is written in terms of the activity of a fundamental component. However, as shown in I, it correctly accounts for the formation of binary, trinary, etc., composite particles. For instance, at very low density the continuum-state interactions are negligible so that Eq. (3) is equivalent to the Saha equation. Since for an n_r-component Saha gas

$$\frac{P}{kT}=\sum_{n=1}^{n_r}\frac{N_n}{V}, \tag{9}$$

where N_n is the number of particles of type n, it must be that $N_n/V = z^n b_n$.

Defining z_n as the n-body bound-state part of $z^n b_n$, so that $z_n \to N_n/V$ as the total density goes to zero, allows one to recast Eq. (3) into a form resembling an n_r-component cluster expansion, i.e.,

$$\frac{P}{kT} = \sum_{n=1}^{n_r} z_n + \sum_{n=1}^{n_r} \sum_{m=1}^{n_r} z_n z_m b^f_{nm} + \cdots , \tag{10}$$

where $z_1 \equiv z$ and the quantity $z_1^2 b_2$ has been divided into its bound and free parts, which are for Boltzmann statistics[3]

$$z_2 = 8 \left(\frac{\pi\hbar^2}{mkT} \right)^{3/2} z_1^2 \sum_{nl} (2l+1) e^{-E_{nl}/kT} , \tag{11}$$

$$z_1^2 b^f_{11} = 8 \left(\frac{\pi\hbar^2}{mkT} \right)^{3/2} z_1^2 \frac{1}{\pi} \times \int_0^\infty \sum_l (2l+1) \frac{d\delta_l}{dp} e^{-p^2/mkT} dp , \tag{12}$$

where E_{nl} is the bound-state energy, p is the relative momentum of a continuum state, and δ_l is the phase shift. Similarly, $z^3 b_3$ is divided into its three-body bound-state sum z_3, the part that involves two particles in a bound state interacting with a third particle in a continuum state $z_1 z_2 b^f_{12}$, and the three-body continuum-state part $z_1^3 b^f_{111}$. The expansion (10) is the desired form for a reacting gas. (To be perfectly general it is necessary to define an activity for each bound state.) The leading term is equivalent to the Saha equation at low density and the correction terms systematically take account of all two-particle, three-particle, etc., scattering interactions that can occur among the various fundamental and composite particles present in the gas at a given V and T. The main purpose of the present paper is to obtain the result equivalent to Eq. (10) that is appropriate for a Coulomb gas.

B. Coulomb gas

In the Coulomb case, each of the cluster integrals diverges in the limit $V \to \infty$, but $S(z)$ exists. Mayer[4] and Abe[5] have shown how to evaluate $S(z)$ by expanding the β_{J-1} in powers of the potential and collecting infinite sums of particular types of terms to obtain a new expansion in which the sum (2), for a one-component Coulomb gas in a uniform background, is replaced by

$$S(z) = S_R + \sum_{n=2}^{\infty} S_n , \tag{13}$$

where

$$S_R = 1/12\pi\lambda_D^3 , \quad \lambda_D^2 = kT/4\pi e^2 z , \tag{14}$$

$$\frac{S_2}{z^2} \equiv s_2 = -B_2(\lambda_D) + \frac{2\pi e^2 \lambda_D^2}{kT} - \frac{\pi}{2} \left(\frac{e^2}{kT} \right)^2 \lambda_D , \tag{15}$$

$$B_2(\lambda_D) = -2\pi \int_0^\infty dr\, r^2 (e^{-u_s/kT} - 1) , \tag{16}$$

$$u_s = e^2 e^{-r/\lambda_D}/r . \tag{17}$$

Each of the higher s_n, which are not explicitly given here, have $-B_n(\lambda_D)/(n-1)$ as their leading term. The s_n of Eq. (13) now replace the Y_J in Eqs. (4)–(6). Since the s_n depend on λ_D, it follows that $\partial s_n/\partial z \neq 0$. This fact considerably complicates Eq. (1) with the result that Eq. (3) is short of terms. It was shown in I that the missing terms can be expressed in terms of a function χ_R, which involves only ring-type diagrams, and the C_n. A partial result for this expression that was obtained in I is

$$\frac{P}{kT} = z + \chi_R + \sum_{n=2}^{\infty} \left(C_n + z \frac{\partial \chi_R}{\partial z} \frac{\partial C_n}{\partial z} + \cdots \right) , \tag{18}$$

where χ_R is the sum of all the terms in Eq. (1) involving S, with S replaced by S_R.

Because of the repulsive nature of the interaction, the one-component gas in a uniform background cannot have bound states. However, for illustrative purposes it is useful to pretend that it does. To eliminate the short-range divergence of the classical cluster coefficients, resulting from the assumed attractive potential, we replace them with their quantum-mechanical analogs. Proceeding as in the ordinary-gas case, C_2 is partitioned into its effective one-body part z_2 and its scattering state two-body part $z_1^2 s_{11}$. The leading terms in the pressure expression, as given by Eq. (18), are

$$\frac{P}{kT} = z_1 + S_R + z_1 \left(\frac{\partial S_R}{\partial z_1} \right)^2 + (z_2 + z_1^2 s_{11}) + 2 \left(\frac{\partial S_R}{\partial z_1} \right) (z_2 + z_1^2 s_{11}) . \tag{19}$$

Since $\partial S_R/\partial z_1$ has a $z_1^{1/2}$ dependence on the activity, the last term of Eq. (19) has a $z_1^{1/2} z_2$ dependence on the activities. The introduction of the composite-particle activity, thus, shows that this term is of the same order as $S_R(z_1)$. In fact it is equal to the first-order term in the Taylor-series expansion of $S_R(z_1 + 2z_2)$. If this result carried through to all orders it would mean that the composite particles enter the plasma interaction in the same way as point charges. For gases involving electrons and nuclei it will be shown later that a Taylor-series expansion of this type does in fact exist, but because of the polarizability of the composite particles there are additional terms. The existence of the Taylor series for the ring-type diagrams amounts to a proof, after the activity is eliminated, that the multicomponent Debye-Huckel term is the leading interaction correction to the ideal-gas pressure for partially ionized gases, i.e.,

$$\frac{P}{kT}=n_e+\sum_i n_i+\frac{1}{12\pi\lambda_D^3}+\cdots, \tag{20}$$

where

$$\lambda_D^2=kT\Big/\left[4\pi e^2\left(n_e+\sum_i Z_i^2 n_i\right)\right],$$

n is the density, and Z_i is the net charge on ions of type i. This is only the simplest example of what we wish to demonstrate.

III. EXTENSION OF THE S AND C EXPANSIONS FOR COULOMB GASES

The demonstration that the Taylor series exists for the electron-nucleus gas requires a more complete two-component form of Eq. (18). To accomplish this it is necessary to first extend the two-component version of the S expansion. Because of the increasing complexity of S_n with increasing n, only those components of S for which $n \leq 4$ will be worked out. To utilize these S_n we will need to work out all terms in the two-component version of Eq. (2) for $m \leq 4$, i.e., all terms involving S four times. By inversion of the virial expansion, as described in I, we obtain the following extended result for the S expansion:

$$\begin{aligned}\frac{P}{kT}={}&z_a+z_b+S+\sum_{i=\{a,b\}}\sum_{m_i=2}^{\infty}\frac{z_i}{m_i}\left(\frac{\partial}{\partial z_i}z_i\right)^{m_i-2}\\&\times\left(\frac{\partial S}{\partial z_i}\right)^{m_i}+z_a z_b\psi_c+\frac{z_a z_b}{2!}\frac{\partial}{\partial z_a}\left(z_a\frac{\partial S}{\partial z_a}\psi_c\right)\\&+\frac{z_a z_b}{2!}\frac{\partial}{\partial z_b}\left(z_b\frac{\partial S}{\partial z_b}\psi_c\right),\end{aligned} \tag{21}$$

where

$$\psi_c=\left(\frac{\partial S}{\partial z_a}\right)\left(\frac{\partial S}{\partial z_b}\right)\left(\frac{\partial^2 S}{\partial z_a\partial z_b}\right).$$

The last two terms of Eq. (21) are new and correspond to the $m=4$ cross terms. It appears from an inspection of the equation that the cross terms can be generated to all orders in a manner similar to those terms that do not involve cross derivatives.

In the multicomponent case the function $S(z)$ is given in terms of the virial coefficients by

$$S(z)=-\sum_{\underline{J}=2}^{\infty}B_{\underline{J}}z^{\underline{J}}/(J-1), \tag{22}$$

where $B_{\underline{J}}z^{\underline{J}}$ signifies a multinominal expansion such that

$$B_{\underline{J}}z^{\underline{J}}=(B_a z_a+B_b z_b+B_c z_c+\cdots)^J$$

with the understanding that $B_\alpha B_\beta B_\gamma\cdots\to B_{\alpha\beta\gamma}\cdots$, e.g., $(B_a z_a+B_b z_b)^2=z_a^2B_{aa}+2z_a z_b B_{ab}+z_b^2 B_{bb}$. The multicomponent generalization of Abe's[5] nodal expansion for a Coulomb gas then gives

$$S(z)=S_R+\sum_{\underline{n}=2}S_{\underline{n}}=S_R+\sum_{ijkm\cdots}S_{ijkm}, \tag{23}$$

where each sum ranges over all types of fundamental charged particles present in the gas. The nodal-expansion expressions for S_n, through $\underline{n}=3$, were given in I. These terms plus the $S_{\underline{4}}$ terms, required in the present analysis, are

$$S_R=1/12\pi\lambda_D^3,$$

$$\lambda_D^2=kT\Big/\left(4\pi e^2\sum_{i=\{a,b,c,\ldots\}}\xi_i^2 z_i^2\right), \tag{24}$$

where ξ_i is the charge on component i;

$$S_{ij}=z_i z_j\left(-B_{ij}(\lambda_D)-2\pi\int_0^\infty r^2\,dr\,(q_{ij}-\tfrac{1}{2}q_{ij}^2)\right), \tag{25}$$

$$S_{ijk}=z_i z_j z_k\left(-\tfrac{1}{2}B_{ijk}(\lambda_D)-\sum_{p=1}^{3}\iint dr_{ij}\,dr_{ik}\,q_{ik}q_{jk}f_{ij}-\frac{2}{3!}\iint dr_{ij}\,dr_{ik}\,q_{ij}q_{jk}q_{ik}\right), \tag{26}$$

$$\begin{aligned}S_{ijkm}=z_i z_j z_k z_m\Bigg(&-\tfrac{1}{3}B_{ijkm}(\lambda_D)-\frac{1}{4!}\sum_{p=1}^{6}\iiint dr_{ij}\,dr_{jk}\,dr_{jm}[q_{jk}q_{km}f_{ij}f_{mi}(f_{jm}+1)+q_{ij}q_{mi}f_{jk}f_{km}(f_{jm}+1)\\&\qquad-q_{ij}q_{jk}q_{km}q_{mi}f_{jm}]\\&-\frac{3}{4!}\iiint dr_{ij}\,dr_{jk}\,dr_{jm}\,q_{ij}q_{jk}q_{km}q_{mi}\Bigg),\end{aligned} \tag{27}$$

where $q_{\alpha\beta}=-\xi_\alpha\xi_\beta e^{-r/\lambda_D}/rkT$, $f_{\alpha\beta}=e^{-q_{\alpha\beta}}-1$, and the sum over p represents the number of permutations for the given structure.

The two-component generalization of Eq. (18) can be obtained in a straightforward, although tedious, way. One simply substitutes Eq. (23) into Eq. (21) and then recognizes that the resultant terms can be expressed in terms of χ_R and $C_{\underline{n}}$ and their derivatives with respect to z. The two-component version of the C expansion, which is sufficient to show convincingly that the aforementioned Taylor series exists, is

$$\frac{P}{kT}=z_a+z_b+\chi_R+\sum_{\underline{n}}\left\{C_{\underline{n}}+\sum_{\substack{k=1\\ l=k-m}}^{\infty}\sum_{m=0}^{k}\frac{z_a^m z_b^l}{(k-m)!}\left[\left(\frac{\partial\chi_R}{\partial z_a}\right)^m\left(\frac{\partial\chi_R}{\partial z_b}\right)^l\frac{\partial^k C_{\underline{n}}}{\partial z_a^m\partial z_b^l}+\frac{\partial^k\chi_R}{\partial z_a^m\partial z_b^l}\left(\frac{\partial C_{\underline{n}}}{\partial z_b}\right)^m\left(\frac{\partial C_{\underline{n}}}{\partial z_b}\right)^l\right]\right\}$$

$$+\sum_{i=\{a,b\}}z_i^3\frac{\partial S_R}{\partial z_i}\frac{\partial^2 S_R}{\partial z_i^2}\frac{\partial C_{\underline{2}}}{\partial z_i}\frac{\partial^2 C_{\underline{2}}}{\partial z_i^2}+\sum_{\substack{ij\\ i\neq j}}z_i^2 z_j\left(\frac{\partial S_R}{\partial z_i}\frac{\partial^2 S_R}{\partial z_i\partial z_j}\frac{\partial C_{\underline{2}}}{\partial z_j}\frac{\partial^2 C_{\underline{2}}}{\partial z_i^2}\right.$$
$$+\frac{\partial S_R}{\partial z_j}\frac{\partial^2 S_R}{\partial z_i^2}\frac{\partial C_{\underline{2}}}{\partial z_i}\frac{\partial^2 C_{\underline{2}}}{\partial z_i\partial z_j}$$
$$\left.+\frac{\partial S_R}{\partial z_i}\frac{\partial^2 S_R}{\partial z_i\partial z_j}\frac{\partial C_{\underline{2}}}{\partial z_i}\frac{\partial^2 C_{\underline{2}}}{\partial z_i\partial z_j}\right)+\cdots, \tag{28}$$

where χ_R is the sum of all terms in Eq. (21) involving S, with S replaced with S_R,

$$C_{\underline{2}}\equiv S_{\underline{2}}=z_a^2 s_{aa}+2z_a z_b s_{ab}+z_b^2 s_{bb}, \tag{29}$$

$$C_{\underline{3}}\equiv S_{\underline{3}}+\frac{z_a}{2!}\left(\frac{\partial S_{\underline{2}}}{\partial z_a}\right)^2+\frac{z_b}{2!}\left(\frac{\partial S_{\underline{2}}}{\partial z_b}\right)^2, \tag{30}$$

$$C_{\underline{4}}\equiv S_{\underline{4}}+z_a\frac{\partial S_{\underline{2}}}{\partial z_a}\frac{\partial S_{\underline{3}}}{\partial z_b}+z_b\frac{\partial S_{\underline{2}}}{\partial z_b}\frac{\partial S_{\underline{3}}}{\partial z_b}$$
$$+\frac{z_a}{3!}\frac{\partial}{\partial z_a}z_a\left(\frac{\partial S_{\underline{2}}}{\partial z_a}\right)^3+\frac{z_b}{3!}\frac{\partial}{\partial z_b}z_b\left(\frac{\partial S_{\underline{2}}}{\partial z_b}\right)^3$$
$$+z_a z_b\frac{\partial S_{\underline{2}}}{\partial z_a}\frac{\partial S_{\underline{3}}}{\partial z_b}\frac{\partial^2 S_{\underline{2}}}{\partial z_a\partial z_b}, \tag{31}$$

and $s_{\alpha\beta\gamma}\equiv S_{\alpha\beta\gamma}/z_\alpha z_\beta z_\gamma$. We have not yet found a general form for the terms of Eq. (28) that explicitly display S_R. In the present work the a component is an electron and the b component is a nucleus, which will be indicated by e and α, respectively.

IV. RECONSTITUTED C EXPANSION

Demonstrating that Eq. (28) is actually a Taylor-series expansion of a similar expansion involving an augmented set of activity variables requires a great deal of tedious manipulation which of course cannot be reproduced here. Instead we will give a short introduction into how to start the analysis, proceed to the final result, and then give further details of how the result was obtained.

A. Preliminary analysis

We first demonstrate the appearance of composite-particle effects in S_R. Consider first the quantum-mechanical expression for s_{ij} [see Eq. (40) of I] obtained by replacing the classical second virial coefficient with its quantum-mechanical equivalent valid in the limit $\lambda/\lambda_D\to 0$, i.e.,

$$s_{ij}=4(\pi\lambda_{ij})^{3/2}\,\mathrm{Tr}(e^{-\beta H_2}-e^{-\beta H_0})$$
$$+2\pi\lambda_D^2\left(\frac{\xi_i\xi_j}{kT}\right)-\frac{\pi}{2}\left(\frac{\xi_i\xi_j}{kT}\right)^2\lambda_D$$
$$=s_{ij}^b+s_{ij}^f, \tag{32}$$

where

$$s_{ij}^b=2^{1/2}\lambda_{ij}^3\sum_{nl}(2l+1)e^{-E_{nl}/kT}, \tag{33}$$

$$s_{ij}^f=\frac{2^{1/2}\lambda_{ij}^3}{\pi}\sum_l(2l+1)\int_0^\infty dp\,\frac{d\delta_l}{dp}\,e^{-p^2/2\mu_{ij}kT}$$
$$+2\pi\lambda_D^2\left(\frac{\xi_i\xi_j}{kT}\right)-\frac{\pi}{2}\left(\frac{\xi_i\xi_j}{kT}\right)^2\lambda_D, \tag{34}$$

where

$$\lambda_{ij}=(\pi\hbar^2/\mu_{ij}kT)^{1/2},$$

μ_{ij} is the reduced mass, s_{ij}^b and s_{ij}^f are the bound- and continuum-state parts, and in the current paper s_{ij} is a member of the set $\{s_{ee}, s_{e\alpha}, s_{\alpha\alpha}\}$. The bound states E_{nl} for the screened Coulomb potential[6] can be expanded in terms of inverse powers of λ_D. After division by kT, the expansion is

$$\frac{E_{nl}}{kT}=-\frac{Z^2e^4\mu_{e\alpha}}{2\hbar^2kT}+\frac{Ze^2}{kT\lambda_D}-\frac{e^2a_{nl}}{kT\lambda_D^2}+\cdots\circ$$
$$=-\frac{Z^2e^4\mu_{e\alpha}}{2\hbar^2kT}+2Z\frac{\partial S_R}{\partial U}-2\frac{\partial S_R}{\partial U}\frac{a_{nl}}{kT}+\cdots, \tag{35}$$

where Z is the charge of the nucleus, the a_{nl} are constants, and $U=Z_e+Z^2z_\alpha$. The first-order correction to E_{nl}/kT is the same for all states and is related to the derivative of S_R according to the second form of Eq. (35). The terms of Eq. (28) also involve derivatives of S_R. This is no coincidence, and is, in fact, the key for reorganization of the C expansion.

Jackson and Klein[7] have concluded that the energy levels of the static screened Coulomb potential are not correct for low-lying states. Instead they find that the energy levels should be shifted by $-Ze^2/\lambda_D$; i.e., the correct energy levels, divided by kT, are

$$E_{nl}^s/kT=E_{nl}/kT-2Z\,\partial S_R/\partial U. \tag{36}$$

It is straightforward to show that the shifted energy levels also enter Eq. (28). Consider the first few terms involving $s_{e\alpha}$. In terms of E_{nl}^s/kT,

$$2s^{b}_{e\alpha}=2(2^{1/2}\lambda^{3}_{e\alpha})\sum_{nl}(2l+1)e^{-E^{s}_{nl}/kT}\,e^{-2Z\,\partial S_R/\partial U}. \tag{37}$$

Now expand the last exponential in $s^{b}_{e\alpha}$ in terms of $2Z(\partial S_R/\partial U)$. The second term in the expansion together with the leading bound state parts of $z_e(\partial S_R/\partial z_e)(\partial C_{\underline{2}}/\partial z_e)$ and $z_\alpha(\partial S_R/\partial z_\alpha)(\partial C_{\underline{2}}/\partial z_\alpha)$ gives

$$(Z-1)^2\frac{\partial S_R}{\partial U}\left[2z_e z_\alpha\left(2^{1/2}\lambda^{3}_{e\alpha}\sum_{nl}(2l+1)e^{-E^{s}_{nl}/kT}\right)\right]. \tag{38}$$

If we define $z_{e\alpha}$ as

$$z_{e\alpha}=2z_e z_\alpha\left(2^{1/2}\lambda^{3}_{e\alpha}\sum_{nl}(2l+1)e^{-E^{s}_{nl}/kT}\right) \tag{39}$$

the expression (38) is equal to the first term in a Taylor-series expansion of $S_R(U+(Z-1)^2z_{e\alpha})$ about $S_R(U)$. In other words, the $-Ze^2/\lambda_D$ shift in the energy levels should be considered as part of the classical electrostatic term arising from the existence of a new species of charge $Z-1$.

The activity, as given by Eq. (39), is a discontinuous function of the interaction strength. This discontinuity is compensated by the zero-energy part of the phase shifts[8] which, after an integration by parts of $s^{f}_{e\alpha}$, subtracts a -1 from each of the terms $e^{-E_{nl}/kT}$. Instead of working with two discontinuous terms it seems desirable to move the phase-shift discontinuity into the definition of $z_{e\alpha}$ so that

$$z_{e\alpha}=2z_e z_\alpha\left(2^{1/2}\lambda^{3}_{e\alpha}\sum_{nl}(2l+1)(e^{-E^{s}_{nl}/kT}-1)\right). \tag{40}$$

Actually each term $\{nl\}$ in the sum $z_{e\alpha}$ represents a separate activity, $z^{nl}_{e\alpha}$, for particles in the state $\{nl\}$.

Higher-order terms in the Taylor-series expansion of $S_R(U+(Z-1)^2z_{e\alpha})$ can, with increasing difficulty, be found in Eq. (28). This can be interpreted as the replacement of $\lambda_D(U)$ with $\lambda_D(U+(Z-1)^2z_{e\alpha})$. More generally it can be shown that this replacement occurs in other types of terms. The final result of this analysis, which includes all terms involving the augmented set of activities through $\frac{5}{2}$ powers, is

$$\frac{P}{kT}=\sum_i z_i+\chi^{*}_{R_3}+C^{*}_{\underline{2}}+\sum_i z_i\frac{\partial S^{*}_{R}}{\partial z_i}\frac{\partial C^{*}_{\underline{2}}}{\partial z_i}-\sum_i z_i\frac{\partial S^{*}_{R}}{\partial z_i}\left(\sum_{nl}\frac{\partial E^{s}_{nl}}{\partial U}z^{nl}_{e\alpha}+\sum_{nln'l'}\frac{\partial E^{s}_{nln'l'}}{\partial U}z^{nln'l'}_{ee\alpha}\right)\Big/kT, \tag{41}$$

where $i\rightarrow\{z_e,z_\alpha,z^{10}_{e\alpha},z^{20}_{e\alpha},\ldots,z^{1010}_{ee\alpha},z^{2010}_{ee\alpha},\ldots\}$, the subscripts e and α refer, respectively, to electrons and nuclei of charge Z,

$$\chi^{*}_{R_3}=S^{*}_{R}+\sum_i\frac{z_i}{2}\left(\frac{\partial S^{*}_{R}}{\partial z_i}\right)^2+\sum_i\frac{z_i}{3!}\frac{\partial}{\partial z_i}z_i\left(\frac{\partial S^{*}_{R}}{\partial z_i}\right)^3+\tfrac{1}{2}\sum_i\sum_{\substack{j\\ i\neq j}}z_i z_j\frac{\partial S^{*}_{R}}{\partial z_i}\frac{\partial S^{*}_{R}}{\partial z_j}\frac{\partial^2 S^{*}_{R}}{\partial z_i\,\partial z_j}, \tag{42}$$

$$S^{*}_{R}=1/12\pi(\lambda^{*}_{D})^3, \tag{43}$$

$$\lambda^{*}_{D}=\left(\frac{kT}{4\pi e^2[z_e+Z^2z_\alpha+(Z-1)^2z_{e\alpha}+(Z-2)^2z_{ee\alpha}\cdots]}\right)^{1/2}, \tag{44}$$

$$z_{ee\alpha}=\sum_{nln'l'}z^{nln'l'}_{ee\alpha}, \tag{45}$$

$$z^{nln'l'}_{ee\alpha}=2z_e z^{nl}_{e\alpha}(2^{1/2}\lambda^{3}_{e\mathrm{H}})(2l+1)\times(e^{-E^{s}_{nln'l'}/kT}-1), \tag{46}$$

$$E^{s}_{nl}(\lambda^{*}_{D})=E_{nl}(\lambda^{*}_{D})-Ze^2/\lambda^{*}_{D}, \tag{47}$$

$$E^{s}_{nln'l'}(\lambda^{*}_{D})=E_{nln'l'}(\lambda^{*}_{D})-(Z-1)e^2/\lambda^{*}_{D}, \tag{48}$$

$E_{nln'l'}$ is the energy of the second electron relative to the energy of the $\{nl\}$ state,

$$C^{*}_{\underline{2}}=\sum_i\sum_j z_i z_j s^{p}_{ij}, \tag{49}$$

and s^{p}_{ij} is the phase-shift-integral part of s_{ij} that results from an integration by parts.[8] Unless there are bound states $s_{ij}=s^{p}_{ij}$. The s_{ij} involving composite particles are similar to Eqs. (25) and (32), except, because of the shielding due to the core electrons, the terms that are subtracted from the virial coefficients are different. These terms will be given later. It should be noted that the composite-particle activities that appear in Eq. (41) involve the screening length λ^{*}_{D}, but, for simplicity of notation the asterisk has been dropped. To avoid confusion between $S_{\underline{2}}$ components and higher $S_{\underline{n}}$ components when i or j or both correspond to composite particles, we will designate the one-electron–nucleus bound states as H instead of $e\alpha$, the two-electron–nucleus bound states as He, etc. Since no confusion arises from the notation $z_{e\alpha}$, $z_{ee\alpha}$, etc., we will continue to use it rather than the corresponding notation z_{H}, z_{He}, etc.

Equation (41) has the same form as Eq. (28) except that it involves an augmented set of activity variables, i.e., one for each fundamental particle and one for each state of each composite particle. The analogy is not exact, however, since the last term of Eq. (41) has no counterpart in Eq. (28). This term is related to the polarizability of the core electrons and is similar to terms appearing in $\chi^*_{R_3}$. It is only the first in a series of terms which have not yet been worked out. The leading z dependence of this term is $z^{5/2}$ so that it is the only one required at the present level of application. Even though Eq. (41) is written in terms of an augmented set of activity variables, z_e and z_α are still the only independent variables. They are determined through the density in the usual way, i.e.,

$$\mathfrak{N}_e = z_e \frac{\partial (P/kT)}{\partial z_e}, \quad \mathfrak{N}_\alpha = z_\alpha \frac{\partial (P/kT)}{\partial z_\alpha}. \tag{50}$$

Inspection of Eqs. (40) and (46) shows that the composite-particle activities appear on both sides of these equations, so that the composite-particle activities must be obtained by iteration at fixed values of z_e and z_α.

At high temperatures where bound states are unimportant, the $z^{5/2}$ expansion of Eq. (28) is identical to that of Eq. (41). However, when the temperature is reduced terms such as $z_e z_{e\alpha} s_{e\mathrm{H}}$, which are of order z^2 in Eq. (41) actually correspond to terms of order z^3 in the expansion of Eq. (28). The terms that comprise the Taylor-series expansion of S^*_R, that are important when various types of composite particles are present, actually come from throughout the entire expansion of Eq. (28). At high density where λ_D is less than $0.84a_0/Z$ there can be no bound states and the two expansions are again identical to all orders in z.

Since the present analysis has avoided quantum-statistical perturbation theory it violates the Pauli principle. At low density this violation is only important when bound states are involved. For the interaction terms in the quantum-statistical problem the violation of the Pauli principle is corrected by the exchange diagrams. We shall not attempt to sum these diagrams here; instead it is assumed that a summation of the exchange diagrams, using the same procedure as for the direct diagrams, will replace the classical $b_n(\lambda_D)$ with their quantum-statistical analogs[9] which involve the spin. This will have no effect on the bound states of $b_{e\alpha}(\lambda_D)$, but will be quite significant for the bound states of $b_{ee\alpha}(\lambda_D)$ since the spin statistical weight when both particles are in the same state is one instead of four, as in the direct case. Consistent with the assumption of low density we ignore exchange corrections to scattering states.

B. Extended analysis

Since $z_{e\alpha} \propto z_e z_\alpha$, $z_{ee\alpha} \propto z_e^2 z_\alpha$ it is apparent that obtaining higher terms in the Taylor-series expansion involving $z^m_{e\alpha}, z^m_{ee\alpha}, \ldots$ come from terms of order $z^{2m}, z^{3m}, \ldots$ in the expansion (28). Because of the increasing complexity of the C_n we will consider in detail only those terms involving $n \leq 4$, although we find it necessary to use some terms for $n > 4$. Consider now the expression for C_3 given by Eq. (30). It has two complications not present in C_2; the S_3 part involves integrals whose quantum-mechanical analogs are not obvious and the S_2 part involves derivatives, which because of the screening-length dependence of S_2, introduce terms not present in the C_n of an ordinary gas.

The terms in S_3 that are subtracted from $-B_3$ can be given quantum-mechanical meaning by using the convolution theorem to transform the integrals, i.e.,

$$\int\int d\vec{r}_{ij}\, d\vec{r}_{ik}\, q_{ij} q_{jk} w_{ik} = \frac{\xi_i \xi_j^2 \xi_k}{(kT)^2} \frac{(4\pi)^4}{2(2\pi)^3} \int\int \frac{dk\, dr\, kr \sin kr}{(k^2 + 1/\lambda_D^2)^2} \left(e^{q_{ik}/kT} - 1 - q_{ik}/kT\right)$$

$$= \frac{4\xi_i \xi_j^2 \xi_k}{(kT)^2} (\pi^2 \lambda_D) \int_0^\infty dr\, r^2 e^{-r/\lambda_D} \left(e^{q_{ik}/kT} - 1 - q_{ik}/kT\right), \tag{51}$$

where $w_{ik} = f_{ik} - q_{ik}/kT$, and the last form comes from an integration over k. The second form of Eq. (51) is recognized as the derivative of s_{ik} with respect to U, with the result

$$\int\int d\vec{r}_{ij}\, d\vec{r}_{ik}\, q_{ij} q_{jk} w_{ik} = 2 \frac{\xi_i \xi_j^2 \xi_k}{e^4} \frac{\partial s_{ik}}{\partial U}. \tag{52}$$

Clearly Eq. (52) is also valid if w_{ik} is replaced with a Slater sum, so that an expression which is valid for both classical and quantum mechanics (in the $\gamma \rightarrow 0$ limit) is

$$S_{ijk} = z_i z_j z_k \left(-\tfrac{1}{2} B_{ijk} - \frac{2}{3!} \sum_{p=1}^{3} \frac{\xi_i \xi_j \xi_k^2}{e^4} \frac{1}{Z} \frac{\partial s_{ij}}{\partial U} + 2\pi^2 \frac{\xi_i^2 \xi_j^2 \xi_k^2}{(kT)^3} \lambda_D^3 \right), \tag{53}$$

where the sum over p indicates there are three permutations. In a similar way the convolution theorem can be applied to transform S_4. Consider the following integral that occurs in Eq. (25):

$$\int\int\int d\vec{r}_{ij}\,d\vec{r}_{jk}\,d\vec{r}_{jm}\,q_{jk}q_{km}f_{ij}\,f_{mi}\,f_{jm}$$

$$=\int d\vec{r}_{jk}q_{jk}\int d\vec{r}_{jm}q_{km}(|\vec{r}_{jm}-\vec{r}_{jk}|)\psi_{jm}, \tag{54}$$

where

$$\psi_{jm}=\int d\vec{r}_{ij}\,f_{ij}\,f_{mi}(|\vec{r}_{jm}-\vec{r}_{ij}|)f_{jm}.$$

It can be transformed by convolution exactly as above. The last term in parentheses in Eq. (26) can also be evaluated by convolution, giving terms involving $\partial^2 s_{ij}/\partial U^2$ and $\partial s_{ij}/\partial U$. These terms will not enter our present analysis since they correspond to states for which two particles are bound and two particles are free; i.e., only effective two-body interactions are considered in the present analysis. The transformed expression for S_{ijkm} is

$$S_{ijkm}=z_i z_j z_k z_m\left(-\tfrac{1}{3}B_{ijkm}-\frac{2}{4!}\sum_{p=1}^{4}\frac{\xi_i\xi_k\xi_m^2}{e^4}\,\frac{1}{Z}\,\frac{\partial B_{ijk}}{\partial U}+\frac{1}{4!}\sum_{p=1}^{6}q_{ij}q_{jk}q_{km}q_{mi}\,f_{jm}-\frac{\pi^3}{4}\,\frac{\xi_i^2\xi_j^2\xi_k^2\xi_m^2}{(kT)^4}\,\lambda_D^5\right). \tag{55}$$

The forms for the S_{ijk} and S_{ijkm} given by Eqs. (53) and (55) make it possible to discuss the $C_{\underline{3}}$ and $C_{\underline{4}}$ in terms of bound states and continuum states, which is a central part of the development being worked out in this paper. It will be useful to divide each of the $C_{\underline{n}}$ into a part corresponds to a cluster coefficient in the ordinary -gas case and a part that results from the fact that $C_{\underline{n}}$ depends on λ_D. These two parts will be denoted by $C_{a,\underline{n}}$ and $C_{b,\underline{n}}$, respectively. The definition of $C_{\underline{3}}$ given by Eq. (30) gives explicitly

$$C_{a,\underline{3}}=z_e^3(s_{eee}+2s_{ee}^2)+z_\alpha^3(s_{\alpha\alpha\alpha}+2s_{\alpha\alpha}^2)+3z_e^2 z_\alpha[s_{ee\alpha}^f+s_{ee\alpha}^b+4s_{ee}(s_{e\alpha}^f+s_{e\alpha}^b)+2(s_{e\alpha}^f+s_{e\alpha}^b)^2]$$

$$+3z_e z_\alpha^2[s_{e\alpha\alpha}^f+s_{e\alpha\alpha}^b+4s_{\alpha\alpha}(s_{e\alpha}^f+s_{e\alpha}^b)+2(s_{e\alpha}^f+s_{e\alpha}^b)^2], \tag{56}$$

$$C_{b,\underline{3}}=\sum_{\substack{i=\{e,\alpha\}\\ j\neq i}} z_i\left[[2z_i s_{ii}+2z_j(s_{ij}^f+s_{ij}^b)]\left(z_i^2\frac{\partial s_{ii}}{\partial z_i}+2z_i z_j\frac{\partial}{\partial z_i}(s_{ij}^b+s_{ij}^f)+z_j^2\frac{\partial s_{jj}}{\partial z_i}\right)\right.$$

$$\left.+\frac{1}{2}\left(z_i^2\frac{\partial s_{ii}}{\partial z_i}+2z_i z_j\frac{\partial}{\partial z_i}(s_{ij}^b+s_{ij}^f)+z_j^2\frac{\partial s_{jj}}{\partial z_i}\right)^2\right], \tag{57}$$

where the superscript b indicates only bound states and the superscript f indicates only continuum states. Terms with no superscript cannot have bound states. Next we divide $C_{a,\underline{3}}$ into a part involving only continuum states, $C_{a,\underline{3}}^f$, and a part that remains involving both bound states and continuum states, $C_{a,\underline{3}}^r$:

$$C_{a,\underline{3}}^f=z_e^3(s_{eee}+2s_{ee}^2)+z_\alpha^3(s_{\alpha\alpha\alpha}+2s_{\alpha\alpha}^2)$$

$$+z_e^2 z_\alpha[3s_{e\alpha\alpha}^f+4s_{ee}\,s_{e\alpha}^f+2(s_{e\alpha}^f)^2]$$

$$+z_e z_\alpha^2[3s_{e\alpha\alpha}^f+4s_{\alpha\alpha}s_{e\alpha}^f+2(s_{e\alpha}^f)^2], \tag{58}$$

$$C_{a,\underline{3}}^r=z_e^2 z_\alpha[3s_{ee\alpha}^r+4s_{ee}\,s_{e\alpha}^b+2s_{e\alpha}^b(2s_{e\alpha}^f+s_{e\alpha}^b)]$$

$$+z_e z_\alpha^2[3s_{e\alpha\alpha}^r+4s_{\alpha\alpha}s_{e\alpha}^b+2s_{e\alpha}^b(2s_{e\alpha}^f+s_{e\alpha}^b)]. \tag{59}$$

In order to express $C_{a,\underline{3}}^r$ in terms of eigenvalues and phase shifts, we need to eliminate the $s_{\underline{n}}$ to obtain an expression in terms of cluster coefficients. This is accomplished with the substitutions

$$s_{e\alpha}^b=-B_{e\alpha}^b, \tag{60}$$

$$s_{e\alpha}^f=-B_{e\alpha}^f-Z\frac{2\pi e^2}{kT}\lambda_D^2-\frac{\pi}{2}Z^2\left(\frac{e^2}{kT}\right)^2\lambda_D, \tag{61}$$

$$s_{ee}=-B_{ee}+2\pi\frac{e^2}{kT}\lambda_D^2-\frac{\pi}{2}\left(\frac{e^2}{kT}\right)^2\lambda_D, \tag{62}$$

$$s_{\alpha\alpha}=-B_{\alpha\alpha}+2\pi Z^2\frac{e^2}{kT}\lambda_D^2-\frac{\pi}{4}Z^4\left(\frac{e^2}{kT}\right)^2\lambda_D, \tag{63}$$

$$s_{ee\alpha}^r=-\frac{B_{ee\alpha}^r}{2}+\frac{2}{3}\,\frac{\partial b_{e\alpha}^b}{\partial U}, \tag{64}$$

$$s_{e\alpha\alpha}^r=-\frac{B_{e\alpha\alpha}^r}{2}+\tfrac{2}{3}Z^2\frac{\partial b_{e\alpha}^b}{\partial U}, \tag{65}$$

where

$$\frac{\partial b_{e\alpha}^b}{\partial U}=\frac{\partial s_{e\alpha}^b}{\partial U}=-2Z\frac{\partial^2 S_R}{\partial U^2}b_{e\alpha}^b-\frac{1}{kT}\sum_{nl}A_{nl}\,b_{e\alpha}^{b,nl},$$

$A_{nl}=\partial E^s/\partial U$, and the $b_{e\alpha}^{b,nl}$ are the individual components of $b_{e\alpha}^b$. The result of these substitutions is

$$C^r_{a,\underline{3}} = z_e^2 z_\alpha \left\{ b^r_{ee\alpha} - \left[4(Z-1)\left(\frac{2\pi e^2}{kT}\right)\lambda_D^2 + 4(Z-1)^2 \frac{\pi}{2}\left(\frac{e^2}{kT}\right)^2 \lambda_D \right] b^b_{e\alpha} - \frac{2}{kT}\sum_{nl} A_{nl}\, b^{b,nl}_{e\alpha} \right\}$$

$$+ z_e z_\alpha^2 \left\{ b^r_{e\alpha\alpha} + \left[4Z(Z-1)\left(\frac{2\pi e^2}{kT}\right)\lambda_D^2 - 4Z^2(Z-1)^2 \frac{\pi}{2}\left(\frac{e^2}{kT}\right)^2 \lambda_D \right] b^b_{e\alpha} - \frac{2Z^2}{kT}\sum_{nl} A_{nl}\, b^{b,nl}_{e\alpha} \right\}, \qquad (66)$$

where $b^r_{ee\alpha}$ and $b^r_{e\alpha\alpha}$ are those parts of $b_{ee\alpha}$ and $b_{e\alpha\alpha}$ for the screened Coulomb potential that remain after the three-body continuum states are removed. This will involve three-body bound states as well as states for which two particles are bound and the third is free.

For equation-of-state purposes the three-body states of interest can be calculated, with sufficient accuracy, from a spherical-symmetric spin-independent two-body potential. (The concept of an effective potential is introduced solely for the purpose of calculational tractability.) By fitting the eigenvalue spectrum for $\lambda_D = \infty$, and solving a two-parameter variational problem for λ_D finite, it is shown in the Appendix that a satisfactory potential for an electron or nucleus interacting with a bound electron-nucleus pair is

$$V_{i\mathrm{H}} = (\xi_i e/r)[(Z-1)e^{-r/\lambda_D} + e^{-1.067Zr/a_0}], \qquad (67)$$

where i is an electron or nucleus, H signifies any electron-nucleus bound pair in the hydrogen isoelectronic sequence, and ξ_i is the charge of an i-type particle. The terms in the brackets of Eq. (66) are seen to correspond to the first- and second-order perturbation terms of $-B_{i\mathrm{H}}$ in direct analogy with Eq. (25). There are no terms subtracted that correspond to first-order perturbation due to the core, and even though the last term in each set of curly brackets in Eq. (66) is of the same type as the second-order terms of $-B_{i\mathrm{H}}$, resulting from the core, these terms do not cancel. Therefore, the analogy with Eq. (25) is not exact. The potential $V_{i\mathrm{H}}$ is only valid when H is in its ground state and we must introduce a new potential for each state (nl) of H. In the present work we will consider, at the numerical level, only singly excited states. This should be a very good approximation since the lowest doubly excited state lies well above the series limit for singly excited states, i.e., more than Z^2 Ryd above the ground-state energy.

When the potential $V^{nl}_{i\mathrm{H}}$ is used to calculate the energy levels and phase shifts of an electron or nucleus relative to H the $b^r_{ee\alpha}$ and $b^r_{e\alpha\alpha}$ parts of the cluster coefficients are given by

$$b^r_{e\alpha i} = (4)2^{1/2}\lambda^3_{e\alpha}\sum_{nl} e^{-E_{nl}/kT} b^{nl}_{i\mathrm{H}}, \qquad (68)$$

where the factor 4 corrects for the fact that not all of the particles are the same and $b^{nl}_{i\mathrm{H}}$ is identical with the second cluster coefficient for the potential $V^{nl}_{i\mathrm{H}}$, except that the factor 4 has been separated out and states for which $nl = n'l'$ have a weight $\frac{1}{4}$ instead of 1. The expression for the $C^r_{e\alpha i}$ becomes

$$C^r_{e\alpha i} = 4 z_e z_\alpha (2^{1/2}\lambda^3_{e\alpha}) \sum_{nl} (2l+1) e^{-E_{nl}/kT} s^{nl}_{i\mathrm{H}}, \qquad (69)$$

where

$$s^{nl}_{i\mathrm{H}} = b^{nl}_{i\mathrm{H}} + (Z-1)2\pi\left(\frac{e\xi_i}{kT}\right)\lambda_D^2$$

$$-(Z-1)^2\frac{\pi}{2}\left(\frac{e\xi_i}{kT}\right)^2\lambda_D - \frac{\xi_i^2}{2kT}A_{nl}. \qquad (70)$$

It is shown in the Appendix that the first-order perturbation energy shift for two electrons interacting with a nucleus through the static screened Coulomb potential is $-2(2Z-1)(\partial S_R/\partial U)$. Proceeding as in Eqs. (36)–(39), we define

$$\frac{E^s_{nl} + E^s_{nln'l'}}{kT} = \frac{E_{nl} + E_{nln'l'}}{kT} - 2(2Z-1)\frac{\partial S_R}{\partial U}.$$

Next the shifted energy levels are substituted into Eq. (69) and the exponential of the first-order shift in the energy levels is expanded. The first term in the expanded form of Eq. (69) together with the leading terms of $z_e(\partial\chi_R/\partial z_e)\partial C_{ee}/\partial z_e$ and $z_e(\partial\chi_R/\partial z_\alpha)\partial C_{ee\alpha}/\partial z_\alpha$ gives

$$(Z-2)^2\frac{\partial S_R}{\partial U}\left(4z_e^2 z_\alpha (2^{1/2}\lambda^3_{e\mathrm{H}})\sum_{nl}(2l+1)e^{-E^s_{nl}/kT}\right.$$

$$\left.\times(2^{1/2}\lambda_{e\mathrm{H}})\sum_{n'l'} e^{-E^s_{nln'l'}/kT}\right). \qquad (71)$$

This collection of terms is analogous to Eq. (38) and is part of the first-order term in the Taylor-series expansion of $S_R(U + (Z-1)^2 z_{e\alpha} + (Z-2)^2 z_{ee\alpha})$ about $S_R(U)$. To be consistent with our previous definition of $z^{nl}_{e\alpha}$ it is convenient to subtract -1 from each $e^{-E^s_{nl}/kT}$ so that

$$z_{ee\alpha} = 2z_e \sum_{nl} z^{nl}_{e\alpha}(2^{1/2}\lambda^3_{e\mathrm{H}})$$

$$\times \sum_{n'l'}(2l'+1)(e^{-E^s_{nln'l'}/kT} - 1). \qquad (72)$$

The -1 subtracted from $e^{-E^s_{nln'l'}/kT}$ comes as before from the zero-energy part of the phase shifts. In a crude way we can see that the -1 subtracted from $e^{-E^s_{nl}/kT}$ is probably present in the phase shifts: Assume that $V_{e\mathrm{H}}^{nl}$ is independent of nl, which is clearly not true in any rigorous sense; then it follows immediately that $b_{ee\alpha}=b_{e\alpha}b_{e\mathrm{H}}$. An application of Levinson's theorem to each cluster coefficient gives the desired result. In any case we can always subtract the proper terms at densities, beyond those of current interest, such that three-body continuum states contribute appreciably to the equation of state.

For later use we write $C_{b,\underline{3}}^{r}$ in terms of the $z_{e\alpha}^{nl}$:

$$C_{b,\underline{3}}^{r}=z_{e\alpha}e^{-4Z\Gamma_z}\sum_{nl}\left(-2Z(1+Z^2-[Z]_{c'})\Gamma_z'+\{(Z-1)^2+2Z-[2Z]_{c'}\}\frac{A_{nl}}{kT}\right)z_{e\alpha}^{nl}+\frac{z_e+Z^4z_\alpha}{2}e^{-4Z\Gamma_z}$$
$$\times\left[\sum_{nl}\left(2\Gamma_z'+\frac{A_{nl}}{kT}\right)z_{e\alpha}^{nl}\right]^2+(1+Z^2)z_{e\alpha}e^{-2Z\Gamma_z}z_{\underline{2}}\frac{\partial C_{\underline{2}}^{f}}{\partial U}-(z_e+Z^4z_\alpha)e^{-2Z\Gamma_z}z_{\underline{2}}\frac{\partial C_{\underline{2}}^{f}}{\partial U}\left[\sum_{nl}\left(2\Gamma_z'+\frac{A_{nl}}{kT}\right)z_{e\alpha}^{nl}\right], \tag{73}$$

where $\Gamma_z\equiv\partial S_R/\partial U$, the prime indicates $\partial/\partial U$, and $[\cdots]_{c'}$ indicates these terms have been taken from $C_{a,ee\alpha\alpha}^{r}$. This rearrangement of terms will prove to be helpful in piecing together the result being sought here.

The analysis of $C_{\underline{4}}$ is similar, but more complicated, than the preceding analysis of $C_{\underline{3}}$. In terms of the $S_{\underline{4}}$, $C_{\underline{2}}$, and $C_{\underline{3}}$ it is

$$C_{\underline{4}}=S_{\underline{4}}+\sum_{i=\{e,\alpha\}}\left[z_i\frac{\partial C_{\underline{2}}}{\partial z_i}\frac{\partial C_{\underline{3}}}{\partial z_i}-\tfrac{1}{3}z_i\left(\frac{\partial C_{\underline{2}}}{\partial z_i}\right)^3-\tfrac{1}{2}z_i^2\frac{\partial C_{\underline{2}}}{\partial z_i}\frac{\partial^2 C_{\underline{2}}}{\partial z_i^2}\right]-z_ez_\alpha\frac{\partial C_{\underline{2}}}{\partial z_e}\frac{\partial C_{\underline{2}}}{\partial z_\alpha}\frac{\partial^2 C_{\underline{2}}}{\partial z_e\partial_\alpha}\;. \tag{74}$$

Only the $C_{a,4}$ term will be considered explicitly:

$$C_{a,\underline{4}}=\sum_{i=\{e,\alpha\}}z_i^4(s_{iii}+6c_{ii}c_{iii}-\tfrac{20}{3}c_{ii}^3)+z_ez_\alpha\sum_{i,j\neq i}z_i^2(4s_{iiij}+4c_{ii}c_{iij}+6c_{ij}c_{iii}+2c_{ij}c_{iij}$$
$$-8c_{ii}^2c_{ij}-\tfrac{8}{3}c_{ij}^3-8c_{ii}^2c_{ij}-8c_{ii}c_{ij}^2)$$
$$+z_e^2z_\alpha^2[6s_{ee\alpha\alpha}+4c_{e\alpha}c_{ee\alpha}+2c_{ee}c_{e\alpha\alpha}+4c_{e\alpha}c_{e\alpha\alpha}+2c_{\alpha\alpha}c_{ee\alpha}-12c_{ee}c_{e\alpha}^2-12c_{\alpha\alpha}c_{e\alpha}^2-8c_{e\alpha}^3-8c_{ee}c_{\alpha\alpha}c_{e\alpha}], \tag{75}$$

where $C_{\underline{n}}=\sum_{\lambda,\mu,\nu}(z_\lambda z_\mu z_\nu\cdots)c_{\lambda\mu\nu\cdots}$ and $\lambda,\mu,\nu\ldots$ each range over (e,α). Consider the $C_{a,ee\alpha\alpha}$ component. Only those parts of $C_{a,ee\alpha\alpha}$ which involve bound states are of interest in the present analysis. From Eqs. (55), (53), and (30) we see that these parts of $s_{ee\alpha\alpha}$ are given by

$$s_{ee\alpha\alpha}^{r}=-\tfrac{1}{3}B_{ee\alpha\alpha}^{r}+2Z^2(2Z-1)\pi(e^2/kT)\lambda_Db_{ee\alpha}^{r}+8Z(1+Z^2)(b_{e\alpha}^{b})^2. \tag{76}$$

Proceeding as in the case of $C_{a,ee\alpha}^{r}$ and $C_{a,e\alpha\alpha}^{r}$, we obtain finally

$$C_{a,ee\alpha\alpha}^{r}=z_e^2z_\alpha^2\left\{b_{ee\alpha\alpha}^{r}+\left[4(Z-1)^2\left(\frac{2\pi e^2}{kT}\right)\lambda_D^2-4\{(Z-1)^4-[4Z^2]_{c'}\}\frac{\pi}{2}\left(\frac{e^2}{kT}\right)^2\lambda_D\right](b_{e\alpha}^{b})^2\right.$$
$$-8[(Z-1)^2+|2Z|]b_{e\alpha}^{b}\sum_{nl}\frac{A_{nl}b_{e\alpha}^{b,nl}}{kT}+\left[2Z(Z-2)\left(\frac{2\pi e^2}{kT}\right)\lambda_D^2-Z^2(Z-2)^2\frac{\pi}{2}\left(\frac{e^2}{kT}\right)^2\lambda_D\right]b_{ee\alpha}^{r}$$
$$\left.-\frac{2Z^2}{kT}\sum_{nln'l'}A_{nln'l'}b_{ee\alpha}^{nln'l'}\right\} \tag{77}$$

where $A_{nln'l'}=\partial E_{nln'l'}/\partial U$. In its present form the terms in the first set of large square brackets subtracted from $b_{ee\alpha\alpha}^{r}$ do not correspond exactly to the first- and second-order perturbation terms for the long-range part of the V_{HH} potential. This is rectified by transferring the $-16Z^2(\pi/2)\times(e^2/kT)^2\lambda_D$ term (indicated by $[\cdots]_{c'}$) to $C_{b,\underline{3}}^{r}$. It will also prove to be convenient to transfer the $-16Zb_{e\alpha}^{b}\sum A_{nl}b_{e\alpha}^{b,nl}/kT$ terms to $C_{b,\underline{3}}^{r}$. The expression for $C_{b,\underline{3}}^{r}$ was written down with these transfers in mind. More generally we will carry out these transfers everywhere these terms appear in the expansion.

In the present analysis only those parts of $b_{ee\alpha\alpha}$ that correspond to two-body interactions between fundamental and composite particles, or between composite particles, are of interest, so that

$$b_{ee\alpha\alpha}^{r}=4(2^{1/2}\lambda_{e\alpha}^3)\sum_{nl}(2l+1)e^{-E_{nl}/kT}(2^{1/2}\lambda_{e\alpha}^3)$$
$$\times\sum_{n'l'}(2l'+1)e^{-E_{n'l'}/kT}b_{\mathrm{HH}}^{nln'l'}$$
$$+8(2^{1/2}\lambda_{e\alpha}^3)\sum_{nl}(2l+1)e^{-E_{nl}/kT}(2^{1/2}\lambda_{e\mathrm{H}}^3)$$
$$\times\sum_{n'l'}(2l'+1)e^{-E_{nln'l'}/kT}b_{\alpha\mathrm{He}}^{nln'l'}, \tag{78}$$

where as before the $b_{\mathrm{HH}}^{nln'l'}$ and $b_{\alpha\mathrm{He}}^{nln'l'}$ are second cluster coefficients for the effective two-body potentials $V_{\mathrm{HH}}^{nln'l'}$ and $V_{\mathrm{He}}^{nln'l'}$ except that they are reduced by the identical particle statistical factor.

$$C_{a,ee\alpha\alpha}^{r}=\sum_{nl} z_{e\alpha}^{nl}\sum_{n'l'} z_{e\alpha}^{n'l'}\, s_{\mathrm{HH}}^{nln'l'}\, e^{-4Z\Gamma_z} +2z_{\alpha}\sum_{nln'l'} z_{ee\alpha}^{nln'l'}\, s_{\alpha\mathrm{He}}^{nln'l'}\, e^{-2(2Z-1)\Gamma_z}, \qquad (79)$$

where again -1 is subtracted from each Boltzmann factor and

$$s_{\mathrm{HH}}^{nln'l'}=b_{\mathrm{HH}}^{nln'l'}+(Z-1)^2\left(\frac{2\pi e^2}{kT}\right)\lambda_D^2 -(Z-1)^4\frac{\pi}{2}\left(\frac{e^2}{kT}\right)^2\lambda_D-\frac{(Z-1)^2}{2kT}(A_{nl}+A_{n'l'}), \qquad (80)$$

$$s_{i\mathrm{He}}^{nln'l'}=b_{i\mathrm{He}}^{nln'l'}+(Z-2)2\pi\left(\frac{e\xi_i}{kT}\right)\lambda_D^2 -(Z-2)^2\frac{\pi}{2}\left(\frac{e\xi_i}{kT}\right)^2\lambda_D-\frac{\xi_i^2}{2kT}A_{nln'l'}. \qquad (81)$$

The i in Eq. (81) $\rightarrow\{e,\alpha\}$ where $s_{e\mathrm{He}}$ comes from $C_{a,eee\alpha}^{r}$. If $Z>2$ then $C_{a,eee\alpha}^{r}$ should be defined in terms of a new activity $Z_{eee\alpha}$ according to the above procedure.

The analysis of $C_{\underline{3}}$ and $C_{\underline{4}}$ provides the basis for proceeding with the demonstration that Eq. (41) is valid. The first few terms in the required derivatives of χ_R are explicitly

$$\frac{\partial\chi_R}{\partial z_i}=Z_i^2\Gamma_z+\tfrac{1}{2}Z_i^4\Gamma_z^2+U\Gamma_z\Gamma_z'+\cdots, \qquad (82)$$

$$\frac{\partial^2\chi_R}{\partial z_i^2}=Z_i^4\Gamma_z'+2Z_i^6\Gamma_z\Gamma_z'+Z_i^6(z_e+Z_i^2Z_j^6z_\alpha)(\Gamma_z')^2 +Z_i^6(z_e+Z_i^2Z_j^6z_\alpha)(\Gamma_z')^2+\cdots, \qquad (83)$$

$$\frac{\partial^2\chi_R}{\partial z_e\partial z_\alpha}=Z^2\Gamma_z'+Z^2\Gamma_z\Gamma_z'+Z^2(z_e+Z^4z_\alpha)(\Gamma_z')^2 +Z^2(z_e+Z^4z_\alpha)\Gamma_z\Gamma_z'', \qquad (84)$$

where $i\rightarrow\{e,\alpha\}$ and $j\neq i$. The first few derivatives of the $C_{\underline{n}}$ are

$$z_i\frac{\partial C_{\underline{2}}}{\partial z_i}=z_i\frac{\partial C_{\underline{2}}^{f}}{\partial z_i}+\left(z_{e\alpha}-2ZZ_i^2z_iz_{e\alpha}\Gamma_z'-Z_i^2z_i\sum_{nl}\frac{A_{nl}z_{e\alpha}^{nl}}{kT}\right)e^{-2Z\Gamma_z}+\cdots, \qquad (85)$$

$$z_i^2\frac{\partial^2 C_{\underline{2}}}{\partial z_i^2}=z_i^2\frac{\partial^2 C_{\underline{2}}^{f}}{\partial z_i^2}+\left(-2z_iz_{e\alpha}\Gamma_z-2Z_i^2z_i\sum_{nl}\frac{A_{nl}z_{e\alpha}^{nl}}{kT}-ZZ_i^4z_i^2z_{e\alpha}\Gamma_z''-Z_i^4z_i^2\sum_{nl}\frac{z_{e\alpha}^{nl}}{kT}+Z_i^6z_j^2z_{e\alpha}(\Gamma_z')^2 -2ZZ_i^4z_i^2\Gamma_z'\sum_{nl}\frac{A_{nl}z_{e\alpha}^{nl}}{kT}\right)e^{-2Z\Gamma_z}, \qquad (86)$$

$$z_ez_\alpha\frac{\partial^2 C_{\underline{2}}}{\partial z_e\partial z_\alpha}=z_ez_\alpha\frac{\partial^2 C_{\underline{2}}^{f}}{\partial z_e\partial z_\alpha}+\left(z_{e\alpha}-ZUz_{e\alpha}\Gamma_z'-U\sum_{nl}\frac{A^{nl}z_{e\alpha}^{nl}}{kT}-Z^3z_ez_\alpha z_{e\alpha}\Gamma_z''+Z^4z_ez_\alpha z_{e\alpha}(\Gamma_z')^2 -z_ez_\alpha(Z+Z^3)\sum_{nl}\frac{A_{nl}z_{e\alpha}^{nl}}{kT}\right)e^{-2Z\Gamma_z}. \qquad (87)$$

The next step is to substitute these expressions in Eq. (28) and collect terms.

The second-order terms in the Taylor-series expansion of $S_R(U+(Z-1)^2z_{e\alpha})$ about $S_R(U)$, i.e., the term $(Z-1)^4\Gamma_z'z_{e\alpha}^2/2$, is composed of the $-2Z(1+Z^2-Z)\Gamma_z'z_{e\alpha}^2$ term from $C_{b,\underline{3}}^{r}$, the $Z_i^4\Gamma_z'z_{e\alpha}^2/2$ terms from $z_i^2(\partial^2\chi_R/\partial z_i^2)(\partial C_{\underline{2}}/\partial z_i)^2$, and the $Z^2\Gamma_z'z_{e\alpha}^2/2$ term from $z_ez_\alpha(\partial^2\chi_R/\partial z_e\partial z_\alpha)(\partial C_{\underline{2}}/\partial z_e)\times(\partial C_{\underline{2}}/\partial z_\alpha)$. At this point all terms of the type $\Gamma_z'z_{e\alpha}^2$ have been accounted for. The third term in the Taylor-series expansion of S_R will involve $C_{\underline{5}}$ terms and has not been worked out. Expansions for the remaining terms of Eq. (41) can also be worked out to the same order of approximation, although we are able to incorporate some parts of the $C_{\underline{n}}$ for $n>4$. In the new expansion we expect that the definition of the screening length should be changed so that it depends on the augmented set of activity variables. If so, terms of the revised expansion, when expanded in a Taylor series about U, must be present in the original expansion, e.g.,

$$z_{e\alpha}(U+(Z-1)^2z_{e\alpha}+(Z-2)^2z_{ee\alpha}+\cdots) =z_{e\alpha}(U)+[(Z-1)^2z_{e\alpha}(U) +(Z-2)^2z_{ee\alpha}(U)+\cdots]\frac{\partial z_{e\alpha}}{\partial U}+\cdots, \qquad (88)$$

which corresponds to a Debye length given by

$$\lambda_D^{*}=\left(\frac{kT}{4\pi e^2(z_e+Z^2z_\alpha+(Z-1)^2z_{e\alpha}+(Z-2)^2z_{ee\alpha})}\right)^{1/2} \qquad (89)$$

The $(Z-1)^2z_{e\alpha}\partial z_{e\alpha}/\partial U$ term in fact corresponds to the small curly bracketed term of $C_{b,3}^{r}$ [Eq. (73)] and presumably this more general definition of $z_{e\alpha}$ can be carried through to any order.

Continuing, as above, the following extensive but incomplete reordering of the terms in Eq. (28) has been obtained:

$$\begin{aligned}\frac{P}{kT} = z_e + z_\alpha + z_{e\alpha}W + z_{ee\alpha} &+ {}^{1}\left\{ S_R + (Z-1)^2\Gamma_z z_{e\alpha}W + (Z-2)^2\Gamma_z z_{ee\alpha} + \frac{(Z-1)^4}{2}\Gamma_z' z_{e\alpha}^2 \right\} \\ &+ {}^{2}\left\{ \tfrac{1}{2}(z_e + Z^4 z_\alpha + (Z-1)^4 z_{e\alpha})\left(1 + \frac{(Z-1)^2 z_{e\alpha}}{U}\right)\Gamma_z^2 \right\} \\ &+ {}^{3}\left\{ \frac{(z_e + Z^6 z_\alpha + (Z-1)^6 z_{e\alpha})}{3!}\Gamma_z^3 + \frac{(z_e + Z^4 z_\alpha + (Z-1)^4 z_{e\alpha})^2}{2}\Gamma_z^2\Gamma_z' \right\} \\ &+ {}^{4}\left\{ (z_e + Z^4 z_\alpha)\Gamma_z \sum_{nl} A_{nl} z_{e\alpha}^{nl}\left(1 + \frac{(Z-1)^2 z_{e\alpha}}{U} + \frac{(Z-1)^4 z_{e\alpha}}{z_e + Z^4 z_\alpha}\right) \right\} + C_{\underline{2}}^* \\ &+ {}^{5}\left\{ \left(z^{\underline{2}} c_{\underline{2}}^{f'} + 2z_e \sum_{nl} z_{e\alpha}^{nl}\frac{\partial s_{eH}^{f,nl}}{\partial U} + 2z_\alpha \sum_{nl} z_{e\alpha}^{nl}\frac{\partial s_{\alpha H}^{nl}}{\partial z_e} \right)(Z-1)^2 z_{e\alpha} \right\} \\ &+ {}^{6}\Big\{ z_e[\Gamma_Z + (Z-1)^2\Gamma_Z' z_{e\alpha}]\frac{\partial C_{\underline{2}}^*}{\partial z_e} + z_\alpha[Z^2\Gamma_z + Z^2(Z-1)\Gamma_z']\frac{\partial C_{\underline{2}}^*}{\partial z_\alpha} \\ &\qquad + (Z-1)^2\Gamma_z\left(2z_e\sum_{nl} z_{e\alpha}^{nl} s_{eH}^{f,nl} + 2z_\alpha \sum_{nl} z_{e\alpha}^{nl} s_{\alpha H}^{nl}\right)\Big\}, \end{aligned} \tag{90}$$

where

$$z_{e\alpha}W = z_{e\alpha}\left(1 - (Z-1)^2 \sum_{nl}\frac{A^{nl} z_{e\alpha}^{nl}}{kT}\right)$$

is the first two terms in the expansion (88) and $A^{nl} = \partial E^s/\partial U$. For reference purposes a label has been put on the upper left of the curly brackets in Eq. (90). The ${}^{1}\{\cdots\}$ terms correspond to the Taylor-series expansion of S_R^* [Eq. (43)]. The terms in ${}^{2}\{\cdots\}$ can be written in the form

$$\sum_{i=(z_e, z_\alpha, z_{e\alpha})} \tfrac{1}{2} z_i \left(\frac{\partial S_R^*}{\partial z_i}\right)^2, \tag{91}$$

which corresponds to the second term of Eq. (42). The terms enclosed by ${}^{3}\{\cdots\}$ are the leading terms in the expansion of the last two parts of $\chi_{R_3}^*$ [see Eq. (42)]. The terms enclosed by ${}^{4}\{\cdots\}$ are part of the last group of terms in Eq. (41). The term $C_{\underline{2}}^*$ corresponds to the $C_{\underline{2}}^*$ of Eq. (49) and is given by

$$\begin{aligned} C_{\underline{2}}^* = z_e^2 s_{ee} + z_e z_\alpha s_{e\alpha}^{p} + z_{\alpha\alpha}^2 s_{\alpha\alpha} + 2z_e \sum_{nl} z_{e\alpha}^{nl} s_{eH}^{p,nl} \\ + 2z_\alpha \sum_{nl} z_{e\alpha}^{nl} s_{\alpha H}^{nl} + \sum_{nl} z_{e\alpha}^{nl} \sum_{n'l'} z_{e\alpha}^{n'l'} s_{HH}^{nln'l'} \\ + 2z_\alpha \sum_{nln'l'} z_{ee\alpha}^{nln'l'} s_{\alpha He}^{nln'l'} + 2z_e \sum_{nln'l'} z_{ee\alpha}^{nln'l'} s_{eHe}^{nln'l'} + \cdots . \end{aligned} \tag{92}$$

Equation (92) is missing the terms s_{HeH} and s_{HeHe} required by Eq. (49). These terms come from $C_{a,5}^r$ and $C_{a,6}^r$, respectively. Their form is already indicated from the above analysis of $C_{\underline{3}}$ and $C_{\underline{4}}$. The terms enclosed by ${}^{5}\{\cdots\}$ are the first terms in the expansion

$$c_{\underline{2}}(U + (Z-1)^2 z_{e\alpha}) = c_{\underline{2}}(U) + (Z-1)^2 z_{e\alpha}\frac{\partial c_{\underline{2}}}{\partial U} + \cdots . \tag{93}$$

The terms in ${}^{6}\{\cdots\}$ are terms in the expansion of

$$\sum_{i=\{z_e, z_\alpha, z_{e\alpha}\}} z_i \left(\frac{\partial S_R^*}{\partial z_i}\right)\left(\frac{\partial C_{\underline{2}}^*}{\partial z_i}\right).$$

On this basis we conclude that Eq. (41) is the correct expression for P/kT when the composite particles are treated on an equal footing with the fundamental particles. In regions where composite particles exist Eq. (41) automatically selects the parts of Eq. (28) which are important. In the present work we have considered in detail only two-body scattering states in the sense that a composite particle represents only one body. All bound states are accounted for and the remainder of the expansion involves only the correct treatment of three- and more-body scattering states. We have thus far ignored two aspects of the problem which may be important in regions where three-body scattering states can be ignored. These are diffraction corrections to the plasma terms (see Appendix B of I) that result from a rigorous quantum-mechanical perturbation treatment of the Coulomb gas, and degeneracy effects that result from quantum statistics. These modifications of the present analysis will be the subject of a later paper.

V. SOME NUMERICAL RESULTS

The reorganization of Eq. (28), which produced Eq. (41), makes it possible to calculate the equation of state of electron-nucleus gases of any Z for general conditions of ionization and dissociation (provided the density is sufficiently low that three-body scattering is not important). The generalization to gases having more than one type of nucleus is straightforward. We will give elsewhere extensive numerical calculations for a variety of gases. In keeping with the tenor of this paper we give only a brief account of these calculations here.

Numerical calculations for hydrogen based on Eq. (28) were given in I. In this case the formation of a hydrogen atom results in a neutral composite particle so that the gas begins to take on the features of an ordinary gas, in which particles interact through short-range potentials. Because of this, it was assumed there that all the $C_{\underline{n}}$ for $n \geqslant 3$ could be calculated in the Coulomb limit, i.e., $\lambda_D \to \infty$. Equation (41) indicates that the formation of hydrogen introduces terms which are $\propto (Z-1)^n$ which are, of course, zero since $Z=1$. Inspection of the terms in Eq. (50) of I shows that the term $(Z-1)^2 \Gamma_z z_{ep}$ (z_{ep} corresponds to $z_{e\alpha}$ with $Z=1$) is properly treated. However, the term $(Z-1)^4 \Gamma_z' z_{ep}^2/2$ is not. This is because we discarded the part coming from $C_{\underline{3}}$ but kept the parts coming from $z_i\,(\partial s_R/\partial z_i)(\partial C_{\underline{2}}/\partial z_i)$, where $i \to \{e, \alpha\}$.

Figure 1 shows PV/N_0kT vs T for hydrogen having a density 0.01 gm/cm^3. The dotted curve is the result given by Eq. (50) of I using the classical static screened potential and no electron degeneracy corrections. The solid curve is the similar result given by Eq. (41) and the dashed curve is the one-level Saha equation with Debye-Hückel corrections. The current calculation and those of I are in substantial agreement down to 7 eV. Below 7 eV the current values of PV/N_0kT lie below those of I and have a slope very similar to the Saha-Debye-Hückel curve. The cusp in the curve obtained in I reflects the inconsistent treatment of the $\Gamma_z' z_{ep}^2$ terms. The calculations for $n < 0.01$ gm/cm^3 given by Eq. (50) of I, and the present calculations are in increasingly better agreement as $n \to 0$, since $\Gamma_z' \to 0$. As a result, the range of validity of the Saha equation with Debye-Hückel corrections is even greater than reported in I. Another aspect of the reconstituted C expansion is that the corrections due to use of the quantum potential, as reported in I, will be diminished. This will be discussed elsewhere.

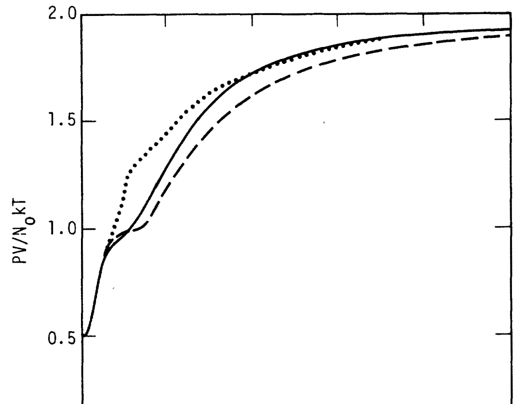

FIG. 1. PV/N_0kT vs T for hydrogen at a density of 0.01 gm/cm^3. Dotted curve is that of Rogers and DeWitt. Solid curve is the result of the current work, and the dashed curve is the result for the one-level Saha equation with Debye-Hückel corrections.

Figure 2 shows PV/N_0kT vs T for helium in the density range $0.000\,01 = n \leqslant 0.1$ gm/cm^3. The bump in the curve separates the ionization (recombination) regions of the first and second electrons similar to the way the bump in Fig. 1 separates the ionization (recombination) and dissociation (association) regions for hydrogen. As the density is increased, the bump becomes less pronounced indicating considerable overlap of the first and second ionization (recombination) ranges. Also the temperature at which recombination starts to occur, as the temperature is reduced, moves to higher temperature as the density is increased. This effect will render the gas considerably less degenerate than a completely ionized gas at the same n and T. It is not plotted, but the one-level (ground state for each species) Saha model with Debye-Hückel corrections lies quite close to those of Fig. 2. Higher-order interaction terms; i.e., those beyond Debye-Hückel, are contributing $\approx 5\%$ at $n=0.1$. Detailed comparisons for the densities considered here and still higher densities will be given elsewhere.

VI. SUMMARY

The long-range divergences present in the cluster expansion of a Coulomb gas were eliminated

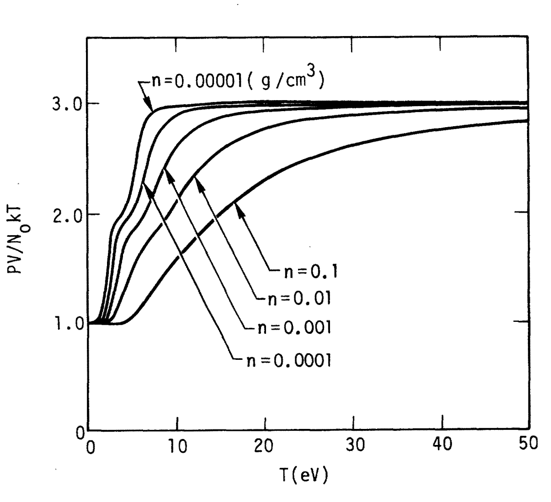

FIG. 2. PV/N_0kT vs T for helium at various densities.

by expressing P/kT in terms of the function $S(z_e, z_\alpha)$, where z_e and z_α are the activities of electrons and nuclei, respectively. A finite result for $S(z_e, z_\alpha)$ was obtained from a multicomponent generalization of the Abe nodal expansion. The expression for P/kT in terms of S is not a systematic expansion in the activities. By introducing some functions C_n, which reduce to cluster coefficients in the ordinary-gas case, an orderly expansion for gases having no composite particles was obtained. However, when composite particles are formed certain terms involving products of z_e and z_α act as though they are of unit power in the activity. To obtain an expansion having orderly convergence properties it was found to be necessary to treat these terms as the activities of composite particles. This introduction of the composite-particle activities greatly simplifies the P/kT expression, since infinite sums of certain types of terms in the fundamental expansion can be recognized as the Taylor-series expansion of analytic functions involving the augmented set of activity variables. As a result $\lambda_D(z_e, z_\alpha)$ in the fundamental expansion is everywhere replaced with $\lambda_D^*(z_e, z_\alpha, z_{e\alpha}, z_{ee\alpha}, \ldots)$, where $z_{e\alpha}$, $z_{ee\alpha}, \ldots$ are the activities of one-electron, two-electron, etc., composite particles.

The analysis given in this paper circumvented quantum-statistical perturbation theory by first working out the classical perturbation result and then replacing those terms which have a classical short-range divergence, due to neglect of the uncertainty principle, with their quantum-statistical mechanical analogs. This procedure is correct in the limit that the ratio $\lambda/\lambda_D \to 0$. For $\lambda/\lambda_D \neq 0$ there are degeneracy and diffraction corrections which will be considered in another place.

ACKNOWLEDGMENTS

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APPENDIX: INTERACTION POTENTIALS

The numerical application of the results of this paper requires the evaluation of some of the cluster coefficients beyond the second. This is an arduous task and, in fact, only very limited calculations of third cluster coefficients have been given.[10] The interest in these papers has been primarily with repulsive potentials that have no bound states, and for which the three-body problem must be handled head on. The existence of bound states allows one to partition the cluster coefficients b_n into equivalent problems involving fewer than n bodies. In the present work we are only extracting those parts of the b_n which are equivalent to a two-body problem. For example, in the case of $b_{ee\alpha}$ we are interested only in those states for which an electron-nucleus bound pair is interacting with the remaining electron.

In the case of two electrons interacting with a nucleus we introduce a two body potential $V_{e\mathrm{H}}$, which is spherically symmetric and spin independent, and show that for equation-of-state purposes the errors introduced by this approximation are not large. In this physical situation the nucleus is partially screened from the second electron so that, for $\lambda_D = \infty$, the potential is composed of the part $-e^2(Z-1)/r$, which cannot be screened, and a part $-e^2 f(Z,r)/r$, where $f(Z,r)$ is a screening function. The screening function is required to reproduce the spectrographic energy levels. Since only spin-independent potentials are to be considered, it is necessary to statistically average the spin splitting of the energy levels, i.e., $E = 3E^{s^3} + E^{s^1}$. We have found that the screening function can be approximated by an exponential $e^{-\eta r}$. If η is selected to give the $(1s)^2$ state of helium accurately, the resulting potential is

$$V_{e\mathrm{H}} = -\frac{e^2}{r}(Z-1) - \frac{e^2}{r} e^{-1.067Zr/a_0}, \qquad \text{(A1)}$$

where H represents any of the ions in the hydrogen isoelectronic sequence. The potential fits the averaged $1s2s$ energy level of helium to within 6%, which is pretty good considering that the $2S^3$ and $2S^1$ energies are split by 20%. However the $2S$ energies are only about $\frac{1}{5}$ the size of the ground-state energy and are thus far less important. Furthermore, the spectrum becomes increasingly hydrogenic with increasing n and l and is correctly reproduced by the long-range part of the potential. The eigenvalues for the ground-state energies of He, Li$^+$, Be^{+2} as calculated from the potential $V_{e\mathrm{H}}$ are given in Table I. The agreement with experiment is good.

The potential (A1) is only valid in the Coulomb limit $\lambda_D \to \infty$, whereas a potential which is valid for any λ_D is required. The eigenvalues and phase shifts for this situation must be obtained from calculations. A variational procedure will be used to obtain the ground state. It is well known that the ground-state energy can be obtained to within a few

TABLE I. Ground-state energies.

n	Calc. Energy (Ry)	Expt. Energy (Ry)
2	1.807	1.807
3	5.650	5.536
4	11.497	11.261

percent from the following two-parameter wave function:

$$\psi = \frac{Z^3}{\sqrt{2}\,\pi(ab)^{3/2}[1+64(ab)^3/(a+b)^3]}\left(e^{-Zr_1/a}e^{-Zr_a/b} + e^{-Zr_1/b}e^{-Zr_2/b}\right). \tag{A2}$$

The resultant energy when all the particles interact through the screened Coulomb potential is (in Ry)

$$\begin{aligned}\frac{E(\lambda_D,Z)}{c} = {} & \frac{Z^2}{2}\left(\frac{1}{a^2}+\frac{1}{b^2}+128\frac{(ab)^2}{(a+b)^6}\right) - Z^2\left(\frac{1}{a(1+a/2Z\lambda_D)^2}+\frac{1}{b(1+b/2Z\lambda_D)^2}+\frac{64(ab)^2}{(a+b)^5[1+ab/Z(a+b)\lambda_D]^2}\right)\\ & + \frac{Za^3d^2}{2b^4}\left[\left(\frac{a\chi_a}{Z\lambda_D}\right)^2 + \left(\frac{b}{a}\right)^3\left(\frac{b\chi_b}{Z\lambda_D}\right)^2 + 2\chi_a + 2\left(\frac{a}{b}\right)^3\chi_b + 8d\chi_a - \frac{8bd\chi_b}{a}\right] - \frac{\chi_a^2\chi_b^2}{\lambda_D}\\ & + \frac{8}{3}\,\frac{Z(ab)^2}{(a+b)^5}\,\chi_{ab}\left[\tfrac{15}{2} + \left(\frac{ab}{Z\lambda_D(a+b)}\right)^2\chi_{ab}(a+12\chi_{ab}+24\chi_{ab}^2)\right] - \frac{64(ab)^3\chi_{ab}^4}{\lambda_D(a+b)^6}\,,\end{aligned} \tag{A3}$$

where a and b are determined from

$$\partial E/\partial a = 0, \quad \partial E/\partial b = 0,$$

and

$$d = [1-(a/b)^2]^{-1}, \quad \chi_a = [1-(a/2Z\lambda_D)^2]^{-1},$$
$$\chi_b = [1-(b/2Z\lambda_D)^2]^{-1}, \quad \chi_{ab} = \{1-[ab/Z\lambda_D(a+b)]^2\}^{-1},$$
$$c = [1+64(ab)^3/(a+b)^6]^{-1}.$$

This gives in the limit $\lambda_D \to \infty$, $E(\infty, 2) = 1.755$ Ry compared to the experimental value 1.807 Ry. The corresponding values for Li^+ are 5.496 and 5.536 Ry.

The first-order energy shift in inverse powers of the potential given by Eq. (A3) is (in Ry)

$$E(\lambda_D, Z) = E(\infty, Z) - (2Z-1)/\lambda_D + \cdots. \tag{A4}$$

This result could easily have been obtained by noting that

$$\frac{e^{-r_{ab}/\lambda_D}}{r_{ab}} = \frac{1}{r_{ab}} - \frac{1}{\lambda_D} + \frac{r_{ab}}{\lambda_D^2} - \cdots, \tag{A5}$$

so that the first-order shift can be obtained from adding up the terms from each interaction. Clearly for N electrons interacting with a nucleus, the first-order shift of the energy of all states is given by

$$E_{\alpha\beta\gamma\ldots}(\lambda_D, Z) = E_{\alpha\beta\gamma\ldots}(\infty, Z) - \sum_{m=1}^{N}\frac{(Z-m)}{\lambda_D}, \tag{A6}$$

where $\alpha\beta\gamma$ are the appropriate quantum numbers.

Since the number of bound states is a function of the screening length, it is of interest to know what these values of the screening length are. Using a one-parameter variational function, we find that $E(\lambda_D, Z) = 0$ at $\lambda_D = 1.26a_0/Z$. The corresponding value given by the best two-parameter wave function is $\lambda_D = a_0/Z$, which is exactly the result given by the best one-parameter wave function for a screened electron-nucleus interaction. The correct value for the screened electron nucleus interaction is[7] $\lambda_D = 0.840a_0/Z$; since the variational energy is a maximum it follows that the critical screening length for the two-electron ground state is $\geq 0.840a_0/Z$ but $< a_0/Z$.

In Fig. 3 the variational energy as a function of screening length for helium is compared with the energy obtained from the following modified form of the potential (A1):

$$V_{i\mathrm{H}} = (\xi_i e/r)(Z-1)e^{-r/\lambda_D} + e^{-1.067Zr/a_0} \tag{A7}$$

It is seen that the potential function gives an energy which agrees with experiment as $\lambda_D \to \infty$ and which is always less than the variational energy, the difference being nearly independent of λ_D. This suggests that the correlation energy is not affected much by screening. Also to a good approximation the core part of the potential depends only slightly on λ_D. The potential (A7) gives zero energy at $\lambda_D \approx 0.78a_0/Z$, which would mean that the two-electron state exists at screening lengths for which the one-electron state does not. This seems obviously wrong. To avoid this problem the screening constant is varied according to

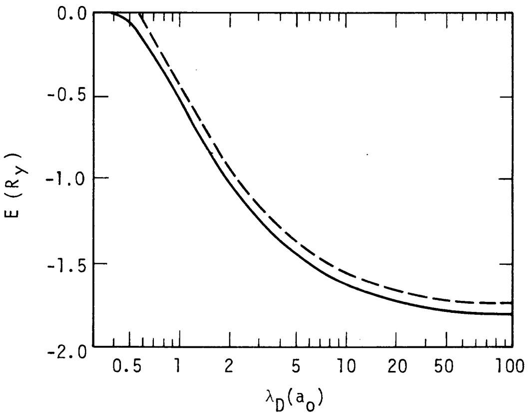

FIG. 3. Ground-state energy vs screening length for He with the Coulomb potential replaced by the screened Coulomb potential. Dashed curve is the energy given by a two-parameter variational calculation, Eq. (A3). Solid curve is the energy obtained by solving the Schrödinger equation for the potential of Eq. (A7). The energy is relative to $E_{1s}(\lambda_D)$.

$$\eta = (1.067 + 0.087/Z^2\lambda_D^2)Z, \tag{A8}$$

so that $\eta = 1/\lambda_D$ at $\lambda_D = 0.840a_0/Z$. In this case the two-electron and one-electron states disappear at the same value of the screening constant. Using electrostatics the potential for a nucleus interacting with a bound electron-nucleus pair is

$$V_{\alpha\text{H}} = -ZV_{e\text{H}}. \tag{A9}$$

The H-H potential can be obtained from the static Klein-Gordon equation[11]

$$\nabla^2 V(r) - V(r)/\lambda_D^2 = -4\pi\rho(r), \tag{A10}$$

which goes to Poisson's equation in the limit $\lambda_D \to \infty$. The charge distribution given by Eq. (A7) is

$$\rho(r) = -Ze\delta(r) + \frac{e}{4\pi}\left(\eta^2 - \frac{1}{\lambda_D^2}\right)\frac{e^{-\eta r}}{r}. \tag{A11}$$

The interaction potential between the two charge distributions can be obtained from

$$V_{\text{HH}}(r) = \int d^3X_1\, d^3X_2\, \rho_1(\vec{r}_1 - \vec{X}_1)\frac{e^{-r/\lambda_D}}{r}\rho_2(\vec{X}_2 - \vec{r}_2), \tag{A12}$$

where $r = |\vec{X}_1 - \vec{X}_2|$. Taking the Fourier transform gives

$$V_{\text{HH}}(r) = \frac{e^2}{2\pi^2}\int d^3k\, e^{-i\vec{k}\cdot\vec{r}}\, F_1(k^2)\frac{1}{(k^2 + 1/\lambda_D^2)}F_2(k^2), \tag{A13}$$

where

$$\begin{aligned} F_i(\vec{k}^2) &= \frac{1}{e}\int d^3r\, e^{i\vec{k}\cdot\vec{r}}\rho_i(r) \\ &= -2Z + (\eta^2 - 1/\lambda_D^2)/(k^2 + \eta^2). \end{aligned} \tag{A14}$$

Integration over k gives

$$\begin{aligned} V_{\text{HH}}(r) = {} & \frac{(Z-1)^2 e^2 e^{-r/\lambda_D}}{r} + \frac{(2Z-1)e^2 e^{-\eta r}}{r} \\ & -\tfrac{1}{2}e^2\eta\left(1 - \frac{1}{(\eta\lambda_D)^2}\right)e^{-\eta r}. \end{aligned} \tag{A15}$$

So again we see that the core potential is not much affected by the screening until $\lambda_D \approx 1/\eta$. This result is very useful and indicates that for still more complex interactions such as He-He we can take advantage of the extensive work that exists on the $\lambda_D = \infty$ effective interaction potential.

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