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# Effective Potential Description of the Quantum Ideal Gases*

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An attempt is made to describe the quantum ideal gases by means of a classical Boltzmann factor using an effective pair potential. We find the $n$-body distribution function for ideal gases of spin 0 and use the $n=2,3$ cases, generalized for spin $s$, with the Born–Green hierarchal relation to obtain an integrodifferential equation for the effective potential. Several numerical solutions for both the Bose–Einstein and Fermi–Dirac ideal gases are presented.

## I. INTRODUCTION

As is well known, symmetrization of the wavefunction in quantum mechanics, required by the indistinguishability of identical particles, leads to effects which are in many ways similar to the effects of an intermolecular potential. Thus, the probability of finding particles close to one another is altered, becoming larger in the case of bosons and smaller in the case of fermions, and one sometimes speaks of a statistical "attraction" between bosons and "repulsion" between fermions. Uhlenbeck and Gropper[1] have studied this statistical effect using the formalism of classical statistical mechanics with an approximate effective potential, valid at high temperatures, to account for the deviations from classical behavior. More recently, Dunn and Broyles[2] have applied well-developed approximations of classical statistical mechanics to the quantum electron gas after first replacing its Slater sum by a Boltzmann factor made up from an effective pair potential. This effective potential approximated the effects of quantum diffraction as well as of symmetry.

Limiting ourselves to the effects of symmetry, we show in this paper how the Born–Green[3] hierarchy may be used to obtain such an effective potential at any temperature. This potential will then allow the results of wavefunction symmetrization in quantum fluids to be described in terms of a classical Boltzmann factor.

In order to isolate the effects of symmetry we will consider here only the quantum ideal gases, for which we will need the one-, two-, and three-body distribution functions. The general $n$-body function is obtained in the next section for particles of zero spin. The desired first three are then special cases and are generalized in Sec. III for particles of arbitrary spin $s$. The integrodifferential equation for the effective potential is obtained in Sec. IV and numerical solutions are presented, for both Bose–Einstein and Fermi–Dirac ideal gases, in Sec. V.

## II. DISTRIBUTION FUNCTIONS FOR PARTICLES OF ZERO SPIN

We consider a system of $N$ spinless particles at the temperature $T$, all of equal mass $m$ and contained in the volume $V$. The canonical partition function $Q_N$ may be written[4]

$$Q_N=(N!\Lambda^{3N})^{-1}\int W_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)d\mathbf{r}_1\cdots d\mathbf{r}_N, \quad (1)$$

where $\Lambda=(h^2/2\pi mkT)^{1/2}$ is the thermal wavelength and $W_N$ is the Slater sum for the $N$-particle system. The $n$-body distribution function $\rho_N^{(n)}$ is defined by

$$\rho_N^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=[(N-n)!\Lambda^{3N}Q_N]^{-1}\times\int W_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N. \quad (2)$$

It will prove convenient to remove the restriction on particle number $N$. This is done in the grand canonical ensemble where the partition function $\Xi$ and distribution functions $\rho^{(n)}$ are given by

$$\Xi=\sum_{N\geq0}z^NQ_N,$$
$$\rho^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=\Xi^{-1}\sum_{N\geq n}z^NQ_N\rho_N^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n), \quad (3)$$

where $z=\exp(\beta\mu)$ and $\mu$ is the chemical potential.

For the case of no interactions between the particles, the Slater sum $W_N$ has the form[4]

$$W_N(\mathbf{r}_1,\cdots,\mathbf{r}_N)=\sum_P(\pm1)^{|P|}\exp[-\pi\Lambda^{-2}\sum_{j=1}^N(\mathbf{r}_j-P\mathbf{r}_j)^2], \quad (4)$$

where $P$ is the particle permutation operator. The sum is over all $N!$ possible permutations and $|P|$ denotes the parity (even or odd) of the permutation $P$. The upper sign will refer throughout to Bose–Einstein sta-

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[1] G. E. Uhlenbeck and L. Gropper, Phys. Rev. **41**, 79 (1932). See also K. Huang, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1963), pp. 216ff.

[2] T. Dunn and A. A. Broyles, Phys. Rev. **157**, 156 (1967).

[3] M. Born and H. S. Green, Proc. Roy. Soc. (London) **A188**, 10 (1947).

[4] See, e.g., J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Chap. 6.

tistics (symmetric case) and the lower sign to Fermi–Dirac statistics (antisymmetric case).

The expression to be evaluated for the quantum ideal gas $n$-body distribution function is then

$$\rho_N^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=[(N-n)!\Lambda^{3N}Q_N]^{-1}\sum_P(\pm1)^{|P|}\times\int\exp[-\pi\Lambda^{-2}\sum_{j=1}^N(\mathbf{r}_j-P\mathbf{r}_j)^2]d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N. \quad (5)$$

For each permutation $P$, the integral in (5) will break up into a product of disconnected ring-type integrals, with each particle index appearing in one and only one ring; the bond linking the adjacent particles $i$ and $j$ on a ring is

$$f_{ij}\equiv f(r_{ij})=\exp(-\pi r_{ij}^2/\Lambda^2). \quad (6)$$

We will call the points $\mathbf{r}_1,\mathbf{r}_2,\cdots,\mathbf{r}_n$ the *root points* of the rings; all other points, called *field points*, are variables of integration. The parity of a ring with $k$ total points is that of $k-1$. Consider a particular permutation in (5), as illustrated in Fig. 1. We write the contribution from this permutation as

$$I_2(\mathbf{r}_1-\mathbf{r}_2)I_1(\mathbf{r}_2-\mathbf{r}_1)I_2(\mathbf{r}_3-\mathbf{r}_3)\cdots I_0(\mathbf{r}_{n-1}-\mathbf{r}_n)I_0(\mathbf{r}_n-\mathbf{r}_{n-1})J_{N-n-m},$$

where $m$ is the total number of field points in the rooted graphs, $J_{N-n-m}$ is the contribution from diagrams with no root points, and $I_l(\mathbf{r}_i-\mathbf{r}_j)$ is a chain beginning at the root point $\mathbf{r}_i$ and ending at the root point $\mathbf{r}_j$, with $l$ field points in between:

$$I_l(\mathbf{r}_i-\mathbf{r}_j)=(\pm1)^l\int f_{is_1}f_{s_1s_2}\cdots f_{s_lj}d\mathbf{r}_{s_1}\cdots d\mathbf{r}_{s_l}. \quad (7)$$

To obtain the total set of such contributions to $\rho_N^{(n)}$ we proceed as follows. First, holding the rooted graphs fixed, we sum over all possible permutations of the remaining $N-n-m$ points. This yields

$$I_2(\mathbf{r}_1-\mathbf{r}_2)I_1(\mathbf{r}_2-\mathbf{r}_1)I_2(0)\cdots I_0^2(\mathbf{r}_n-\mathbf{r}_{n-1})\sum_P(\pm1)^{|P|}\int\exp[-\pi\Lambda^{-2}\sum_{j=1}^{N-n-m}(\mathbf{r}_j-P\mathbf{r}_j)^2]d\mathbf{r}_1\cdots d\mathbf{r}_{N-n-m}$$
$$=I_2(\mathbf{r}_1-\mathbf{r}_2)I_1(\mathbf{r}_2-\mathbf{r}_1)I_2(0)\cdots I_0^2(\mathbf{r}_n-\mathbf{r}_{n-1})(N-n-m)!\Lambda^{3(N-n-m)}Q_{N-n-m},$$

where we have used (1) and (4). We then sum over all possible arrangements of the $n+m$ points in the rooted graphs and finally over all possible values of $m$; that is,

$$\rho_N^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=[(N-n)!\Lambda^{3N}Q_N]^{-1}\sum_{m=0}^{N-n}\sum_{\substack{\{l_i\}\\(\sum_{i=1}^n l_i=m)}}\frac{(N-n)!}{(N-n-m)!}\times\sum_{P'}(\pm1)^{|P'|}I_{l_1}(\mathbf{r}_1-P'\mathbf{r}_1)I_{l_2}(\mathbf{r}_2-P'\mathbf{r}_2)\cdots I_{l_n}(\mathbf{r}_n-P'\mathbf{r}_n)(N-n-m)!\Lambda^{3(N-n-m)}Q_{N-n-m} \quad (8)$$

$$=Q_N^{-1}\sum_{m=0}^{N-n}\sum_{\substack{\{l_i\}\\(\sum l_i=m)}}\sum_{P'}(\pm1)^{|P'|}\prod_{i=1}^n\{I_{l_i}(\mathbf{r}_i-P'\mathbf{r}_i)\}Q_{N-n-m}\Lambda^{-3(n+m)}, \quad (9)$$

where the permutations $P'$ are over the indices 1 through $n$ and $(N-n)!/(N-n-m)!$ in (8) is the number of ways the $m$ field points of the rooted graphs may be chosen. Then in the grand canonical ensemble we have

$$\rho^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=\Xi^{-1}\sum_{N=n}^{\infty}z^N\sum_{m=0}^{N-n}\sum_{\substack{\{l_i\}\\(\sum l_i=m)}}\sum_{P'}(\pm1)^{|P'|}\prod_{i=1}^n\{I_{l_i}(\mathbf{r}_i-P'\mathbf{r}_i)\}Q_{N-n-m}\Lambda^{-3(n+m)}$$
$$=\sum_{P'}(\pm1)^{|P'|}\prod_{i=1}^n\{\sum_{l=0}^{\infty}I_l(\mathbf{r}_i-P'\mathbf{r}_i)z^{l+1}\Lambda^{-3(l+1)}\}. \quad (10)$$

The sum over $l$ can be evaluated in the following way. Expanding $f(r)$, given by (6), in a Fourier series in a box of volume $V$, we write

$$f(r)=V^{-1}\sum_{\mathbf{k}}f_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r}), \quad (11)$$

where

$$f_{\mathbf{k}}=\int \exp\left(-\frac{\pi r^2}{\Lambda^2}-i\mathbf{k}\cdot\mathbf{r}\right)d\mathbf{r}$$
$$=\Lambda^3 \exp(-\Lambda^2k^2/4\pi). \tag{12}$$

We get then for $I_l$, from (7),

$$I_l(\mathbf{r}_i-\mathbf{r}_j)=(\pm1)^l V^{-1}\sum_{\mathbf{k}} f_{\mathbf{k}}^{l+1}\exp(i\mathbf{k}\cdot\mathbf{r}_{ij}), \tag{13}$$

so that

$$\sum_{l=0}^{\infty} z^{l+1}\Lambda^{-3(l+1)}I_l(\mathbf{r})=V^{-1}\sum_{\mathbf{k}}\{\sum_{l=0}^{\infty}(\pm1)^l(z\Lambda^{-3}f_{\mathbf{k}})^{l+1}\}\exp(i\mathbf{k}\cdot\mathbf{r})$$
$$=V^{-1}\sum_{\mathbf{k}}[z^{-1}\exp(\Lambda^2k^2/4\pi)\mp1]^{-1}\exp(i\mathbf{k}\cdot\mathbf{r})$$
$$=V^{-1}\sum_{\mathbf{k}} n_{\mathbf{k}}\exp(i\mathbf{k}\cdot\mathbf{r})\equiv\eta(\mathbf{r})=\eta(r), \tag{14}$$

where

$$n_{\mathbf{k}}=[z^{-1}\exp(\Lambda^2k^2/4\pi)\mp1]^{-1}. \tag{15}$$

Thus, returning to (10) we find that the ideal gas $n$-body distribution function is given by

$$\rho^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=\sum_P(\pm1)^{|P|}\prod_{i=1}^{n}\eta(\mathbf{r}_i-P\mathbf{r}_i), \tag{16}$$

with $\eta(\mathbf{r})$ defined by (14) and (15). In particular, the first three distributions are

$$\rho^{(1)}(\mathbf{r}_1)=\eta(0)=V^{-1}\sum_{\mathbf{k}} n_{\mathbf{k}}\equiv\rho,$$
$$\rho^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=\eta^2(0)\pm\eta^2(r_{12}),$$
$$\rho^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=\eta^3(0)\pm\eta(0)\eta^2(r_{12})\pm\eta(0)\eta^2(r_{23})\pm\eta(0)\eta^2(r_{31})+2\eta(r_{12})\eta(r_{23})\eta(r_{31}). \tag{17}$$

The expression for $\rho^{(1)}$ is just the well-known[5] relation between $z$ and the number density $\rho=\bar{N}/V$, where $\bar{N}$ is the average number of particles in the system; $n_{\mathbf{k}}$ is the average number in the $\mathbf{k}$th momentum state. The two-body function $\rho^{(2)}$ was first obtained by London[6] and independently by Placzek.[7]

We define for convenience the correlation functions $g^{(n)}$ such that

$$\rho^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=\rho^n g^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n). \tag{18}$$

In particular, we use

$$g^{(2)}(\mathbf{r}_1,\mathbf{r}_2)=1\pm D^2(r_{12}),$$
$$g^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=1\pm D^2(r_{12})\pm D^2(r_{23})\pm D^2(r_{31})+2D(r_{12})D(r_{23})D(r_{31}), \tag{19}$$

where

$$D(r)=\eta(r)/\eta(0). \tag{20}$$

## III. DISTRIBUTION FUNCTIONS FOR PARTICLES OF NONZERO SPIN

Let $\bar{N}_s$ be the average number of identical particles in an ideal gas enclosed in a volume $V$ and let the spin of each particle be $s$. Each particle can then have $2s+1$ different spin orientations. Since particles with different spin orientations are distinguishable, we may consider the ideal gas of $\bar{N}_s$ particles to be made up of $2s+1$ independent ideal gases, each having $\bar{N}_0=\bar{N}_s/(2s+1)$ spinless particles. We wish to find the effects of the spin on the correlation functions of the previous section.

Two cases must be distinguished for the two-particle function $g_s^{(2)}(r_{12})$, in that Particles 1 and 2 may have the same or different spin orientations. (We will denote the correlation functions for particles of spin $s$ by a subscript $s$.) Let Particle 1 have any spin orientation. Then the probability that Particle 2 will have the same spin orientation is given by the fraction $[\bar{N}_s(2s+1)^{-1}-1]/(\bar{N}_s-1)$ and the probability that they will be found a distance $r_{12}$ apart is given by $g_0^{(2)}(r_{12})$, Eq. (19). The fraction of particles having other spin orientations, $[\bar{N}_s-\bar{N}_s(2s+1)^{-1}]/(\bar{N}_s-1)$,

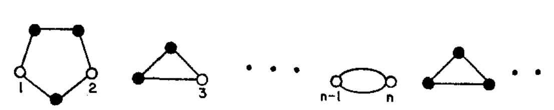


FIG. 1. Result of a particular permutation of the integrand in Eq. (5).

[5] See, e.g., K. Huang, Ref. 1, pp. 197ff.
[6] F. London, J. Chem. Phys. 11, 203 (1943).
[7] G. Placzek, Proc. Berkeley Symp. Mathematical Statistics Probability, 2nd Berkeley, 1950, 581 (1951).

TABLE I. Comparison of the exact values of the internal energy of the quantum ideal gases with the values computed by means of the effective potential. Here $T_B$ is the Bose–Einstein condensation temperature and $T_F$ the Fermi temperature; $z=\exp(\beta\mu)$, where $\mu$ is the chemical potential.

| Bosons | | | | Fermions | | | |
|---|---|---|---|---|---|---|---|
| $T/T_B$ | $z$ | $E/NkT_B$ Exact | $E/NkT_B$ Computed | $T/T_F$ | $z$ | $E/NkT_F$ Exact | $E/NkT_F$ Computed |
| 10.0 | 0.08022 | 14.781 | 14.781 | 4.0 | 0.09721 | 6.100 | 6.099 |
| 5.0 | 0.2150 | 7.189 | 7.190 | 2.0 | 0.2921 | 3.140 | 3.140 |
| 3.0 | 0.4203 | 4.096 | 4.099 | 1.0 | 0.9788 | 1.697 | 1.694 |
| 2.0 | 0.6634 | 2.502 | 2.510 | 0.5 | 4.420 | 1.022 | 1.013 |
| 1.5 | 0.8511 | 1.669 | 1.689 | 0.3 | 21.09 | 0.7872 | 0.7696 |
| 1.1 | 0.9895 | 0.959 | 1.022 | 0.2 | 124.3 | 0.6915 | 0.6634 |

is the probability of the second case mentioned above. Thus the pair correlation function $g_s^{(2)}$ for particles of spin $s$ is given by

$$g_s^{(2)}(r_{12})=g_0^{(2)}(r_{12})\,\frac{\bar{N}_s(2s+1)^{-1}-1}{\bar{N}_s-1}+\frac{\bar{N}_s-\bar{N}_s(2s+1)^{-1}}{\bar{N}_s-1}$$

$$=\frac{2s+g_0^{(2)}(r_{12})}{2s+1},\qquad(21)$$

where we have neglected terms of order $\bar{N}_s^{-1}$. This result was obtained previously by Placzek.[7]

To find $g_s^{(3)}$ we must distinguish three cases: (a) All three particles have the same spin orientation. This occurs with the probability

$$[\bar{N}_s(2s+1)^{-1}-1][\bar{N}_s(2s+1)^{-1}-2]/(\bar{N}_s-1)(\bar{N}_s-2).$$

(b) Two of the particles have the same spin orientation, the third being different. This can occur in three combinations with the weight

$$[\bar{N}_s(2s+1)^{-1}-1][\bar{N}_s-\bar{N}_s(2s+1)^{-1}]/(\bar{N}_s-1)(\bar{N}_s-2)$$

for each. Finally, (c) all three particles may be in different spin states, occurring with a probability

$$[\bar{N}_s-\bar{N}_s(2s+1)^{-1}]\times[\bar{N}_s-2\bar{N}_s(2s+1)^{-1}]/(\bar{N}_s-1)(\bar{N}_s-2).$$

Multiplying each case by the proper correlation function and neglecting terms of order $\bar{N}_s^{-1}$, we arrive at the desired relation,

$$g_s^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)=(2s+1)^{-2}[g_0^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)+2sg_0^{(2)}(r_{12})+2sg_0^{(2)}(r_{23})+2sg_0^{(2)}(r_{31})+2s(2s-1)],\qquad(22)$$

where $g_0^{(2)}$ and $g_0^{(3)}$ are the correlation functions for spinless particles given without subscript in (19).

It is clear that the effect of spin is a reduction of spatial correlations in the ideal gases, due to an increase in distinguishability.

## IV. EQUATION FOR THE EFFECTIVE POTENTIAL

We will begin by assuming the existence of a function $v=v(r;T,\rho_s)$ such that the Slater sum $W_N$ of an ideal gas may be replaced by the Boltzmann factor $\exp(-\beta\sum_{i<j}v_{ij})$, where $v_{ij}=v(r_{ij};T,\rho_s)$, $r_{ij}$ is the separation between molecules $i$ and $j$, and $\beta=1/kT$. Then the $n$-particle distribution function is given by

$$\rho_s^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=\Xi^{-1}\sum_{N\geq n}z^N[(N-n)!\Lambda^{3N}]^{-1}\int\exp(-\beta\sum_{i<j}v_{ij})d\mathbf{r}_{n+1}\cdots d\mathbf{r}_N,\qquad(23)$$

where

$$\Xi=\sum_{N\geq0}z^N[N!\Lambda^{3N}]^{-1}\int\exp(-\beta\sum_{i<j}v_{ij})d\mathbf{r}_1\cdots d\mathbf{r}_N.\qquad(24)$$

Operating on both sides of (23) with $\nabla_1$ we find that $v$ must satisfy the Born–Green relation[3]

$$-\nabla_1\ln\rho_s^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)=\sum_{j=2}^{n}\nabla_1\beta v_{1j}+[\rho_s^{(n)}(\mathbf{r}_1,\cdots,\mathbf{r}_n)]^{-1}\int\nabla_1\beta v_{1,n+1}\rho_s^{(n+1)}(\mathbf{r}_1,\cdots,\mathbf{r}_{n+1})d\mathbf{r}_{n+1}.\qquad(25)$$

In particular, for $n=2$ we have

$$-\nabla_1\ln\rho_s^{(2)}(r_{12})=\nabla_1\beta v(r_{12})+[\rho_s^{(2)}(r_{12})]^{-1}\int\nabla_1\beta v(r_{13})\rho_s^{(3)}(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3)d\mathbf{r}_3.\qquad(26)$$

With the known distribution functions, (26) becomes an integrodifferential equation for the effective potential $v$

in an ideal gas of identical particles of spin $s$. It may be written, after some simplification,

$$\nabla_1\beta v(r_{12}) = -\nabla_1 \ln g_s^{(2)}(r_{12}) - [\rho_s/g_s^{(2)}(r_{12})] \int \nabla_1\beta v(r_{13})[\pm(2s+1)^{-1}D^2(r_{23}) + 2(2s+1)^{-2}D(r_{12})D(r_{23})D(r_{31})]d\mathbf{r}_3, \tag{27}$$

where we have used the fact that

$$\int \nabla_1 v_{13} d\mathbf{r}_3 = 0 = \int \nabla_1 v_{13} D_{13}^2 d\mathbf{r}_3, \tag{28}$$

a result of spatial symmetry. Further, the integrand in (27) is symmetric about $\mathbf{r}_{12}$, so that only the component of $\mathbf{r}_{13}$ parallel to $\mathbf{r}_{12}$ will contribute. We may then write

$$\frac{d\beta v(r_{12})}{dr_{12}} = -\frac{d \ln g_s^{(2)}(r_{12})}{dr_{12}} - \frac{\rho_s}{(2s+1)g_s^{(2)}(r_{12})} \int \cos\theta \frac{d\beta v(r_{13})}{dr_{13}} \left[\pm D^2(r_{23}) + \frac{2}{2s+1} D(r_{12})D(r_{23})D(r_{31})\right] d\mathbf{r}_3, \tag{29}$$

where $\theta$ is the angle between $\mathbf{r}_{12}$ and $\mathbf{r}_{13}$. Using two-center coordinates and defining

$$w(r) = r[d\beta v(r)/dr],$$

$$h(r) = -r[d \ln g_s^{(2)}(r)/dr],$$

$$K(r, t) = -[g_s^{(2)}(r)]^{-1} \int_{|r-t|}^{r+t} \left[\pm D^2(q) + \frac{2}{2s+1} D(r)D(t)D(q)\right] \frac{r^2+t^2-q^2}{2rt} q dq, \tag{30}$$

we have finally

$$w(r) = h(r) + 2\pi\rho_0 \int_0^\infty K(r, t) w(t) dt, \tag{31}$$

where $h$ and $K$ are known functions and $\rho_0 = \rho_s/(2s+1)$.

For small values of $\rho_0\Lambda^3$, we may neglect the second term on the right of (31) and so get approximately

$$\beta v(r) \approx -\ln[1 \pm D^2(r)/(2s+1)] \tag{32}$$

$$\approx -\ln\left[1 \pm \frac{\exp(-2\pi r^2/\Lambda^2)}{2s+1}\right], \tag{33}$$

where we have further approximated $D(r)$ in (33) by neglecting in it terms of order $\rho_0\Lambda^3$. Equation (33) gives the effective potential used by Uhlenbeck and Gropper,[1] with an additional spin factor.

More generally, (31) may be solved numerically for $w(r)$ at any temperature; a final integration then gives the effective potential. Several such solutions are presented in the next section for both Fermi–Dirac and Bose–Einstein ideal gases.

## V. NUMERICAL RESULTS

The method of solution of (31) is by iteration. We note that in evaluating $\eta(r)$, given by (14) and (15), the sum over $\mathbf{k}$ is replaced by an integral according to the prescription

$$V^{-1} \sum_{\mathbf{k}} \to \frac{1}{(2\pi)^3} \int d\mathbf{k}.$$

In the case of bosons, this will limit the resulting equations to the region above the Bose–Einstein condensation. The proper value of $z$ for a given temperature and density is obtained from the first of Eqs. (17).

In the case of a Bose–Einstein gas, we choose units of distance and temperature as follows:

$$a_B = (2.612/\rho_0)^{1/3},$$

$$T_B = h^2/(2\pi mka_B^2), \tag{34}$$

where $\rho_0 = \rho_s/(2s+1)$ and $\rho_s$ is the total density of the system with spin $s$; $T_B$ is seen to be the condensation temperature of a Bose–Einstein ideal gas of density $\rho_0$. Equation (31) was solved for a system of bosons at the reduced temperatures $T/T_B = 10$, 5, 3, 2, 1.5, and 1.1 and zero spin, $s=0$. The pair correlation functions $g_0^{(2)}(r)$ and computed effective potentials $\beta v(r)$ are shown in Figs. 2 and 3 for these cases. We note that as the temperature is reduced the effective potential becomes weaker and of longer range.

For a Fermi–Dirac gas, convenient units are

$$a_F = (6\pi^2\rho_0)^{-1/3},$$

$$T_F = \hbar^2/(2mka_F^2); \tag{35}$$

$kT_F$ is the Fermi energy. We have obtained solutions of (31) for a system of ideal Fermi–Dirac particles of spin $\frac{1}{2}$ at the reduced temperatures $T/T_F = 4$, 2, 1, 0.5, 0.3, and 0.2. These computed functions $\beta v(r)$ and the pair functions $g_{1/2}^{(2)}(r)$ are shown in Figs. 4 and 5. Again a spreading of the effective potential is noted

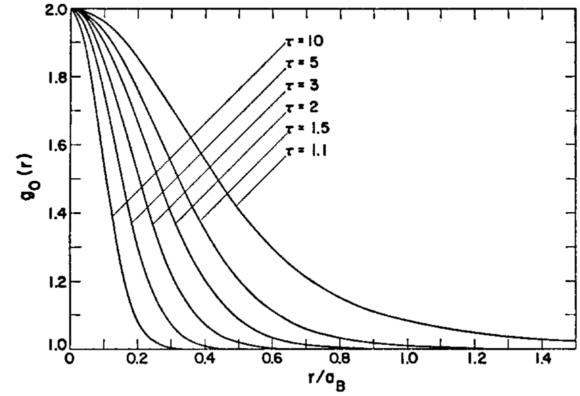


FIG. 2. Pair correlation functions $g_0^{(2)}(r)$ for an ideal gas of spinless bosons. The reduced temperature $\tau$ is in units of the Bose–Einstein condensation temperature, $\tau = T/T_B$.

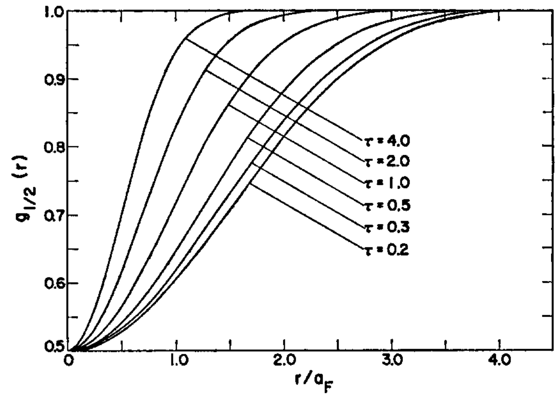


FIG. 4. Pair correlation functions $g_{1/2}^{(2)}(r)$ for an ideal gas of spin $\frac{1}{2}$ fermions. The reduced temperature $\tau$ is in units of the Fermi temperature, $\tau = T/T_F$.

for decreasing $T$. In terms of $v$ alone, the potential also becomes progressively weaker as it becomes longer ranged.

The purpose of finding these effective potentials is to allow the quantum symmetry effects to be included in more complicated problems in a form analogous to the methods of classical statistical mechanics.[2] An initial test of the validity of this approach may be made by using the effective potentials found here to compute thermodynamic quantities of the ideal gases by means of the classical expressions and comparing these with the known answers. Thus for a system described by the partition function of Eq. (24), we define the pressure conveniently as the grand canonical average of the canonical pressure[8]

$$p/kT = \partial \ln \Xi / \partial V \tag{36}$$

and obtain the usual expression

$$\frac{pV}{\bar{N}_s kT} = 1 - \frac{1}{6}\rho_s \int_0^\infty r \frac{d\beta v(r)}{dr} g_s^{(2)}(r) 4\pi r^2 dr, \tag{37}$$

while for the quantum ideal gases the equation of state

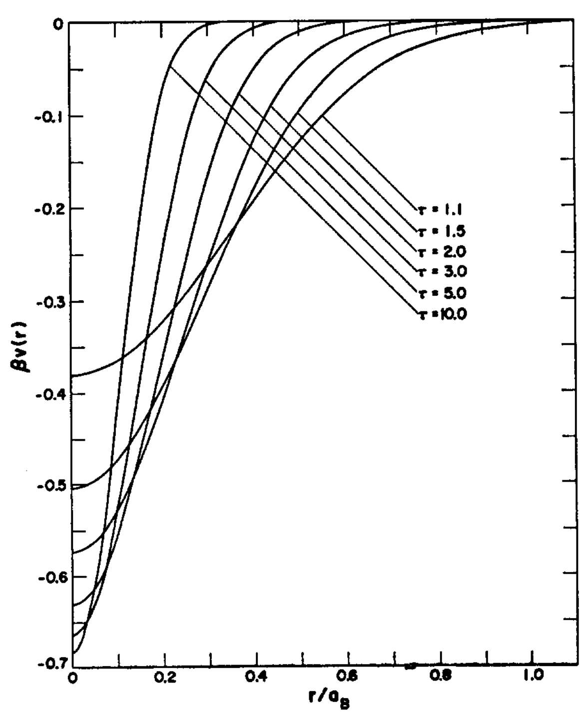


FIG. 3. Computed effective potentials, in units of $kT$, corresponding to the boson $g$'s of Fig. 2.

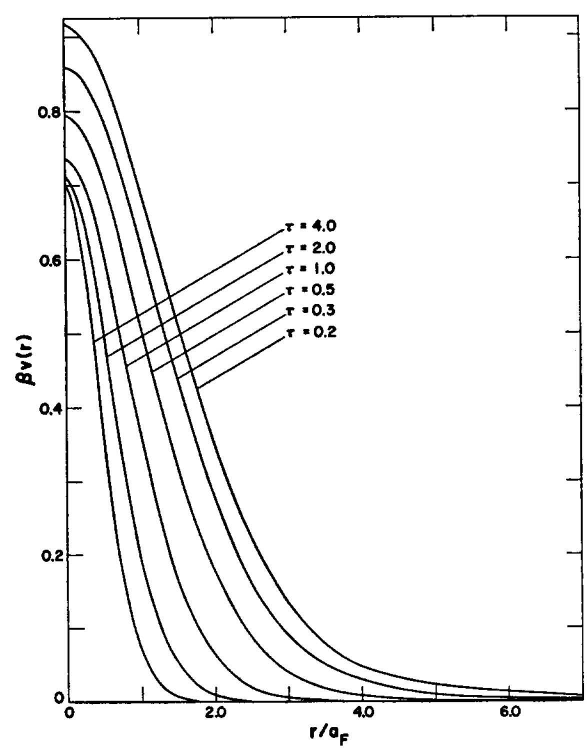


FIG. 5. Computed effective potentials, in units of $kT$, corresponding to the fermion $g$'s of Fig. 4.

[8] T. L. Hill, *Statistical Mechanics* (McGraw-Hill Book Co., New York, 1956), p. 237.

is known to be given by[5]

$$\frac{pV}{\bar{N}_e kT}=\frac{1}{\rho_0\Lambda^3}\frac{8}{3\sqrt{\pi}}\int_0^\infty \frac{ze^{-x^2}}{1\mp ze^{-x^2}}x^4dx. \tag{38}$$

A comparison of computed values from these two equations, for the reduced temperatures cited above, is shown in Table I in the form of the reduced energy per particle, where for both the exact and computed quantities we have identically

$$E=\tfrac{3}{2}pV. \tag{39}$$

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# SCF–MO–LCAO–CI Studies of the Pi-Electronic Structures of Acrolein and Glyoxal Using Ohno's Resonance Integral Formula and Constrained to Satisfy Koopmans' Theorem Exactly

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The pi-electronic structures of the *trans* and *cis* diastereomers of acrolein are studied within the framework of the Pople–Pariser–Parr approximation in which: (1) Resonance integrals are evaluated by a formula originally derived by Ohno, (2) valence-state ionization potentials of non-carbon atoms are chosen by the constraint that Koopmans' theorem is satisfied literally for the first ionization potential of the molecule, and (3) all penetration integrals are neglected. The effects of including nonnearest-neighbor resonance integrals and of using "fixed" effective atomic charges in lieu of "self-consistent electronegativity" values are investigated. Also examined is the effect of modifying Ohno's resonance integral formula when used for heteropolar bonds. The optimum agreement between calculations and the limited experimental evidence available occurs when "self-consistent electronegativity" effective atomic charges are used along with nonnearest-neighbor resonance integrals computed from a modified Ohno formula. Application of the "best" acrolein procedures to the glyoxal molecule suggests either that one cannot use the modified Ohno formula to obtain good spectroscopic intervals and reasonable charge densities from a single set of parameters unless the Koopmans' theorem constraint is relaxed or else that the experimental upper limit to the ionization potential is in error by 0.5 eV or more.

## INTRODUCTION

The notation and formalism of the present work is identical with that of a previous paper[1] (hereafter referred to as Paper I) treating the pi-electronic structure of the formaldehyde molecule. We now wish to extend the earlier procedure to more complicated systems, in particular to systems containing more than one bond type (i.e., both C–O and C–C bond types), so that some indication as to the general reliability and usefulness of the approach is revealed. The ultimate goal of this and the previous paper is to place the parameter problem of the Hückel approximation and its generalizations onto a systematic (and, perhaps, simple) basis.

In Paper I the pi-electronic structure of formaldehyde was investigated by the wellknown Pople–Pariser–Parr approximation[2] along with two innovations, viz., the obtaining of a self-consistent resonance integral by use of Ohno's formula,[3]

$$\beta_{rs}=\tfrac{1}{2}(N_r+N_s)\Delta_{rs}(\gamma_{rs}-2\kappa/d_{rs}), \tag{1}$$

and the requirement that the valence-state ionization potential of the oxygen atom be chosen such that Koopmans' theorem is satisfied exactly for the first ionization potential of the molecule. The self-consistency of the resonance integral $\beta_{rs}$ arises from the fact that the overlap integral $\Delta_{rs}$ depends upon the effective atomic charges which, in turn, depend upon the elements of the first-order density matrix (except for the case of "fixed" effective atomic charges, in which case $\beta_{rs}$ is not self-consistent but also fixed). The two-electron repulsion integrals $\gamma_{rs}$ also depend (but weakly) upon the effective atomic charges if one uses Paoloni's formula for the one-center integrals. The $\gamma_{rs}$ values used in Paper I and in the present work were calculated by the Pariser–Parr charged sphere and quadratic extrapolation procedure although a far simpler formula proposed by Ohno[3] leads to essentially the same numerical values. As in Paper I the number

[1] F. L. Pilar, J. Chem. Phys. **47**, 884 (1967).

[2] J. A. Pople, Trans. Faraday Soc. **49**, 1375 (1953); R. Pariser and R. G. Parr, J. Chem. Phys. **21**, 466, 767 (1953).

[3] K. Ohno, Theoret. Chim. Acta **2**, 219 (1964).