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# Quantum Mechanical Perturbation Expansion for the Second Virial Coefficient and the Ursell–Mayer Function*

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Starting from a quantum mechanical diagrammatic expansion of the grand partition function $\Xi$, and of the coefficients $Vb_l$ in the activity expansion of $\Xi$, and making a term by term passage to the limit of classical nuclear motion, results in a corresponding diagrammatic expansion of the Ursell functions $U_l(\mathbf{R}_1, \cdots, \mathbf{R}_l)$. Presently only the expansion of the Ursell–Mayer function $f(R)$ has been explicitly examined and the terms up to second order perturbation theory, including exchange, have been evaluated. The truncated expansion gives a reasonably accurate expression of $f(R)$ for long and medium range distances ($R \geq 4a_0$) and within this range can be transformed, to the same order of accuracy, into the classical standard form $f(R) = \exp[-u(R)] - 1$, although in principle an exact formulation in such a form is not necessarily possible.

## I. INTRODUCTION

An exact quantum mechanical definition of the second virial coefficient, or of the second coefficient in the activity expansion of the pressure of a gas, is given by

$$Vb_2 = \mathrm{Tr}[\exp(-\beta\bar{H}) - \exp(-\beta\bar{H}_0)], \tag{1}$$

where $\bar{H}$ is the Hamiltonian of a pair of interacting molecules, $\bar{H}_0$ is the Hamiltonian of a pair of noninteracting molecules and where the trace on the rhs of (1) is understood as taken over the states of $\bar{H}$ and $\bar{H}_0$, respectively.

In the following we shall restrict our discussion to monoatomic gases and use (1) as a starting point to obtain a direct perturbation expansion of $b_2$. Then, passing over to the limit of classical motion of the nuclei we obtain $b_2$ in the form

$$b_2/b_1^2 = \tfrac{1}{2}\int f(R)\, d^3R, \tag{2}$$

where $Vb_1$ is the partition function of a single atom. [An explicit expression for it will be obtained in the following (Eq. 47) for a simplified atomic model.] In this classical limit the perturbation expansion turns into an expansion of the Ursell–Mayer function $f(R)$. Using a truncated expansion as an approximation to $b_2$ can be considered then as an alternative to the standard method of taking the classical definition of the Ursell–Mayer function

$$f(R) = \exp[-\beta u(R)] - 1, \tag{3}$$

and substituting for $u(R)$ an approximate expression of the potential energy.

However the two methods do not, in principle, converge to the same result. In fact Zwanzig[1] has already shown, by considering the partition function of a system of atoms in the limit of classical nuclear motion, that definition (3) must be replaced by a more general one where the potential $u(R)$ is replaced by a free energy $u(R, \beta)$ defined by

$$\exp[-\beta u(R, \beta)] = \sum_n \exp[-\beta u_n(R)], \tag{4}$$

where the sum extends over all electronic states (in the sense of the Born–Oppenheimer approximation) of the two atoms separated by a distance $R$. If it were permissible to retain only the ground state term $n=0$ from the sum in (4) we could regain (3). This however holds only provided one can assume that for all relevant $R$ values, i.e., for all $R$ for which $u_0(R) \lesssim kT$, the excited states potential curves lie high, compared to $kT$, above the ground state so that curve crossing or almost crossing does not occur. [For $R$ values outside this range (4) would approach zero quickly and contribute nothing to $f(R)$.]

Thus the presently developed perturbation expansion provides a direct expansion of the Ursell–Mayer function $f(R)$ which is exact in a well-defined classical limit, whereas the method based on the substitution of a potential energy function into (3) is in principle of more restricted accuracy.

In the following we shall evaluate terms in the expansion up to and including second order. The resulting truncated expansion provides a closed expression for $f(R)$ which is valid for long and medium range distances ($R \geq 4a_0$). To the same order of accuracy it is also possible to reexpress $f(R)$ in the form (3), thus defining an intermolecular potential $u(R)$ for this range of $R$. For shorter distances, however, the truncated expansion does not suffice for an accurate or even a qualitatively correct representation of $f(R)$, and consideration of higher order terms or of a different resummation procedure is required.

The presently developed method is not restricted to the second virial coefficient. Indeed in the same manner as in (1) we can write an exact quantum mechanical expression for the "cluster integrals" $b_l$,

$$Vb_l = \mathrm{Tr}\{ \sum_s (-1)^{s-1}(s-1)! \times \sum_{(ls)} \exp[-\beta(\bar{H}_{l_1}+\cdots+\bar{H}_{l_s})]\}, \quad (5)$$

where the sum over $(l_s)$ on the rhs is extended over all possible decompositions of $l$ identical molecules into $s$ sets $l_1, l_2, \cdots, l_s$ and $\bar{H}_{l_i}$ is the full Hamiltonian of such a set of $l_i$ molecules. The trace of each term on the rhs of (5) is understood as taken over all quantum states of independent sets $l_1, \cdots, l_s$ but divided by the correct symmetry number, i.e., by the number of all permutations of equivalent sets. [We refrain here from discussing the necessary corrections to (5) when continuum states of the single molecules contribute significantly to the trace.]

As an extension of what was said about $b_2$ (again considering only monoatomic gases), there exists as well a perturbation expansion for (5) in the limit where the motion of the nuclei is treated classically and we obtain then an expansion for an $l$'th order Ursell function $U_l(\mathbf{R}_1, \cdots, \mathbf{R}_l)$ satisfying

$$Vb_l/b_1^l = (l!)^{-1} \int \cdots \int U_l(\mathbf{R}_1, \cdots, \mathbf{R}_l) d^3\mathbf{R}_1 \cdots d^3\mathbf{R}_l. \quad (6)$$

However this Ursell function does not coincide with the standard classical definition[2]

$$U_l(\mathbf{R}_1, \cdots, \mathbf{R}_l) = \sum_s (-1)^{s-1}(s-1)! \times \sum_{\{ls\}} \exp[-\beta(u^{(l_1)}+\cdots+u^{(l_s)})], \quad (7)$$

where $u^{(m)}(\mathbf{R}_1, \cdots, \mathbf{R}_m)$ is the potential energy of $m$ atoms [and where the sum over $(l_s)$ now extends over all possible decompositions of $l$ distinct atoms into $s$ sets]. In a correct expression these potentials should be replaced by free energies $u^{(m)}(\mathbf{R}_1, \cdots, \mathbf{R}_m, \beta)$ defined by[1]

$$\exp[-\beta u^{(m)}(\mathbf{R}_1, \cdots, \mathbf{R}_m, \beta)] = \sum_n \exp[-\beta u_n^{(m)}(\mathbf{R}_1, \cdots, \mathbf{R}_m)], \quad (8)$$

where $u_n^{(m)}(\mathbf{R}_1, \cdots, \mathbf{R}_m)$ is the $n$'th electronic level of the set of $m$ atoms whose nuclei are fixed at positions $\mathbf{R}_1, \cdots, \mathbf{R}_m$. The possibility that the excited states in (8) cannot be neglected because of (near) crossing of potential surfaces is much more likely here than in the case of pair interactions and the validity of substituting (7) into (6) is less certain than that of substituting (3) into (2).

We wish to note in passing that the problem of the necessity of replacing potentials by free energies has been posed also by Linder in his studies[3] of temperature dependent potentials. There the temperature dependence follows as a consequence of the existence of several low lying (compared to $kT$) excited states of the separate molecules. For such a pair (group) of molecules in several different excited states there correspond several different potential curves (surfaces) which lie near to each other. In fact presently all excited states of the separate molecules are taken into account in the traces in (1) and (5). However our restricted consideration of a stable monoatomic gas whose atoms have high excitation energies practically excludes the contribution of the excited states of the separate molecules to these traces.

## II. DIAGRAMMATIC EXPANSION

Equation (1) and more generally Eq. (5) represent infinite sums of terms in a previously developed perturbation expansion[4] of the log of the grand partition function $\Xi$. The expansion of each term in the sum[2]

$$\log\Xi = V \sum_l z^l b_l \quad (9)$$

is derived from a double expansion of the terms on the rhs of (5). The first is a straightforward Dyson expansion of each of the operators $\exp(-\beta\bar{H}_m)$. The second follows from the method of writing the trace as a sum over the states of $\bar{H}_m$, $|\alpha\rangle$ say, and each of these states in terms of $m$ ordered atomic states $|\alpha_1, \cdots, \alpha_m)$. Since the states $|\alpha\rangle$ are antisymmetric with respect to permutations of the electrons (we ignore throughout our discussion nuclear exchange), we have

$$|\alpha\rangle = A\,|\alpha_1, \cdots, \alpha_m), \quad (10)$$

where $A$ is an antisymmetrizing operator which permutes electron coordinates of different atoms. It decomposes into a sum of permutation operators of an increasing degree of complexity.

For the purpose of the Dyson expansion the Hamiltonian $\bar{H}_m$ is split into

$$\bar{H}_m = \bar{H}_{m0} + \bar{V}_m,$$

with the perturbation $\bar{V}$, which is the intermolecular interaction energy operator, given in the form of

$$\bar{V}_m = \sum_{1\leq a<b\leq m} \int\int [\bar{\rho}_a(\mathbf{x})\bar{\rho}_b(\mathbf{y})/|\mathbf{x}-\mathbf{y}|] d\mathbf{x}d\mathbf{y}, \quad (11)$$

where the sum is extended over all pairs of molecules and where $\bar{\rho}_a(\mathbf{x})$ etc., is a charge density operator of the $a$'th etc, molecule. In a coordinate representation it is given by

$$\bar{\rho}_a(\mathbf{x}) = \sum_{i\epsilon a} e_i \delta(\mathbf{x}_i - \mathbf{x}),$$

where $e_i$, $\mathbf{x}_i$ are, respectively, charge and coordinates of the $i$'th particle and the sum extends over all particles in the molecule. By substituting (11) into the Dyson expansion we obtain a series of terms (diagrams) which are integrals containing as integrands the following types of factors.

The intramolecular correlation functions

$$\bar{f}(\mathbf{x}_1, \tau_1; \cdots; \mathbf{x}_s, \tau_s) = \mathrm{Tr}\{\exp(-\beta\bar{H})T[\bar{\rho}(\mathbf{x}_1, \tau_1) \cdots \bar{\rho}(\mathbf{x}_s, \tau_s)]\}. \quad (12)$$

Here

$$\bar{\rho}(\mathbf{x},\tau)=\exp(\tau\bar{H})\bar{\rho}(\mathbf{x})\exp(-\tau\bar{H}), \tag{13}$$

where $\bar{\rho}(\mathbf{x})$ and $\bar{H}$ are, respectively, the charge density operator and Hamiltonian of a molecule, and the trace is carried over all the molecular states. $T$ is an ordering operator of factors into a sequence with decreasing $\tau$'s $(0\leq\tau_i\leq\beta)$. In diagrammatic notation the intramolecular correlation is represented by a big circle [see Fig. 1(a)] with $s$ variable connection points $\mathbf{x}_1$, $\tau_1$; $\cdots$; $\mathbf{x}_s$, $\tau_s$ assigned to it. These are end points of interaction lines which represent the Coulomb interaction factors $|\mathbf{x}_i-\mathbf{x}_j|^{-1}$ connecting pairs of points at two different molecules, having the same variable $\tau$ assigned to them.

The additional expansion in terms of electron permutation operators leads to additional terms (diagrams) which include as factors also intramolecular correlations of the type

$$\begin{aligned}\bar{f}(\mathbf{x}_1,\tau_1;\cdots;\mathbf{x}_s,\tau_s;\boldsymbol{\xi}_1,\cdots,\boldsymbol{\xi}_r,\boldsymbol{\eta}_1,\cdots,\boldsymbol{\eta}_r)&\\ =\mathrm{Tr}\{\exp(-\beta H)T[\bar{\rho}(\mathbf{x}_1,\tau_1)\cdots\bar{\rho}(\mathbf{x}_s,\tau_s)&\\ \times\Phi_e^+(\boldsymbol{\xi}_1)\cdots\Phi_e^+(\boldsymbol{\xi}_r)\Phi_e(\boldsymbol{\eta}_1)\cdots\Phi_e(\boldsymbol{\eta}_r)]\},&\quad(14)\end{aligned}$$

where $\Phi_e^+(\boldsymbol{\xi})$, $\Phi_e(\boldsymbol{\eta})$, etc., are, respectively, electron creation and annihilation operators. These intramolecular correlations are represented by big circles [see Figs. 1(b), 1(c)] having in addition to $s$ connection points at variable $\tau$'s $r$ pairs of connection points at $\tau=0$. Each one of the latter points $\boldsymbol{\xi}$ or $\boldsymbol{\eta}$, which is assigned to either a creation or annihilation operator, is identified with one other connection point on a different big (molecular) circle but with the assignment to a creation or annihilation operator exchanged. The identification is represented diagrammatically by a wavy line joining the two connection points. It should be noted that for $r$ greater than the number of electrons in the molecule (14) is identically zero, so that exchange diagrams of more than $r$ pairs of electrons can be excluded.

Finally, adding a factor $z$ to each big circle we obtain for the full expansion of log $\Xi$ the sum of all connected diagrams described above. In addition each term $Vz^lb_l$ in (9) is given by the sum of all connected diagrams consisting of exactly $l$ big circles. In particular we can see that the diagrammatic expansion of $b_2$ consists of the sum of all diagrams of two big circles connected either by a "ladder" of Coulomb interaction lines [Fig. 1(a)] or by pairs of electron exchange lines [Fig. 1(c)], or by a combination of both types of connection lines [Fig. 1(b)].

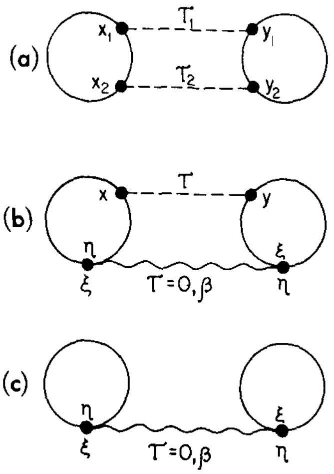

FIG. 1. Diagram representation of typical terms in the expansion of $f(R)$. (a) Second order Coulomb interaction; (b) first order Coulomb plus exchange interaction; (c) pure exchange interaction between two atoms.

## III. SEPARATION OF THE NUCLEAR MOTION

In the following we again restrict ourselves to the case of a monoatomic gas and we will show that when the temperature is sufficiently high ($\beta$ small) but yet low so that $kT$ is small compared to the electronic excitation energy of an atom, each term in the expansion of log $\Xi$, or of the $b_l$, goes over to a definite limiting form. Moreover also each factor of the type (12) or (14) in a diagram goes over to a definite limiting form. This will be seen by writing all state functions and vectors of an atom in terms of the quantum numbers $n$, $\mathbf{K}$, where $n$ refers to the electronic state of the atom and $\mathbf{K}$ is the linear momentum of the atom, or with sufficient accuracy, if the nucleus.Thus let $|n,\mathbf{K}\rangle$ be the state vector of an atom having $Z$ electrons, and its eigenfunction

$$\begin{aligned}\langle\mathbf{R},\mathbf{x}_1,\cdots,\mathbf{x}_Z\,|\,n,\mathbf{K}\rangle=V^{-1/2}&\\ \times\exp(i\mathbf{K}\mathbf{R})\psi_n(\mathbf{x}_1-\mathbf{R},\cdots,\mathbf{x}_Z-\mathbf{R}),&\quad(15)\end{aligned}$$

where $\psi_n(\mathbf{r}_1,\cdots,\mathbf{r}_Z)$ is the electronic eigenfunction of the atom with the electrons' coordinates taken relative to the position $\mathbf{R}$ of the nucleus, and $V$ is the volume of the vessel containing the atom.

Let us examine the matrix elements of the operator $\bar{\rho}(\mathbf{x})$. This operator splits into the sum

$$\bar{\rho}(\mathbf{x})=\bar{\rho}_e(\mathbf{x})+\bar{\rho}_\nu(\mathbf{x}), \tag{16}$$

where $\bar{\rho}_e(\mathbf{x})$ and $\bar{\rho}_\nu(\mathbf{x})$ are, respectively, the electronic and nuclear charge density operator. Hence noting (15) we obtain the matrix elements

$$\begin{aligned}\langle n\mathbf{K}\,|\,\bar{\rho}(\mathbf{x})\,|\,n'\mathbf{K}'\rangle&=\langle n\mathbf{K}\,|\,\bar{\rho}_e(\mathbf{x})\,|\,n'\mathbf{K}'\rangle+\langle n\mathbf{K}\,|\,\bar{\rho}_\nu(\mathbf{x})\,|\,n'\mathbf{K}'\rangle\\ &=-eZ\int\langle n,\mathbf{K}\,|\,\mathbf{R},\mathbf{x},\mathbf{x}_2,\cdots,\mathbf{x}_Z\rangle\langle\mathbf{R},\mathbf{x},\mathbf{x}_2,\cdots,\mathbf{x}_Z\,|\,n'\mathbf{K}'\rangle d\mathbf{x}_2\cdots d\mathbf{x}_r d\mathbf{R}\\ &\quad+eZ\int\langle n,\mathbf{K}\,|\,\mathbf{x},\mathbf{x}_1,\mathbf{x}_2,\cdots,\mathbf{x}_Z\rangle\langle\mathbf{x},\mathbf{x}_1,\cdots,\mathbf{x}_Z\,|\,n'\mathbf{K}'\rangle d\mathbf{x}_1\,d\mathbf{x}_2\cdots d\mathbf{x}_r\\ &=-(eZ/V)\int\exp[i(\mathbf{K}'-\mathbf{K})\mathbf{R}]\psi_n^*(\mathbf{x}-\mathbf{R},\mathbf{x}_2-\mathbf{R},\cdots,\mathbf{x}_2-\mathbf{R})\psi_{n'}(\mathbf{x}-\mathbf{R},\mathbf{x}_2-\mathbf{R},\cdots,\mathbf{x}_2-\mathbf{R})\\ &\quad\times d\mathbf{x}_2\cdots d\mathbf{x}_Z d\mathbf{R}+(eZ/V)\delta_{nn'}\exp[i(\mathbf{K}'-\mathbf{K})\mathbf{x}].\qquad(17)\end{aligned}$$

Defining charge density operators relative to the center of mass of the atom

$$\rho(\mathbf{r})=\rho_e(\mathbf{r})+\rho_\nu(\mathbf{r}), \tag{18}$$

in terms of their matrix elements

$$\langle n\mid\rho_e(\mathbf{r})\mid n'\rangle=-eZ\int\psi_n^*(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_Z)\psi_{n'}(\mathbf{r},\mathbf{r}_2,\cdots,\mathbf{r}_Z)d\mathbf{r}_2\cdots d\mathbf{r}_Z, \tag{19}$$

and

$$\langle n\mid\rho_\nu(\mathbf{r})\mid n'\rangle=eZ\delta_{nn'}\delta(\mathbf{r}), \tag{20}$$

we can rewrite the last equality of (17) in the form

$$\langle n\mathbf{K}\mid\bar{\rho}(\mathbf{x})\mid n'\mathbf{K}'\rangle=V^{-1}\int\langle n\mid\rho(\mathbf{x}-\mathbf{R})\mid n'\rangle\exp[i(\mathbf{K}'-\mathbf{K})\mathbf{R}]d\mathbf{R}. \tag{21}$$

In the same fashion we also obtain the matrix elements

$$\begin{aligned}\langle n\mathbf{K}\mid\Phi_e^+(\boldsymbol{\xi}_1)\cdots\Phi_e^+(\boldsymbol{\xi}_r)\Phi_e(\boldsymbol{\eta}_1)\cdots\Phi_e(\boldsymbol{\eta}_r)\mid n'\mathbf{K}'\rangle&=(Z)_r\int\cdots\int\psi_n^*(\boldsymbol{\xi}_1-\mathbf{R},\cdots,\boldsymbol{\xi}_r-\mathbf{R},\mathbf{x}_{r+1}-\mathbf{R},\cdots,\mathbf{x}_Z-\mathbf{R})\\&\quad\times\psi_{n'}(\boldsymbol{\eta}_1-\mathbf{R},\cdots,\boldsymbol{\eta}_r-\mathbf{R},\mathbf{x}_{r+1}-\mathbf{R},\cdots,\mathbf{x}_Z-\mathbf{R})\exp[i(\mathbf{K}'-\mathbf{K})\mathbf{R}]d\mathbf{x}_{r+1}\cdots d\mathbf{x}_Zd\mathbf{R}\\&\equiv\int\cdots\int\langle n\mid G_e(\boldsymbol{\xi}_1-\mathbf{R},\cdots,\boldsymbol{\xi}_r-\mathbf{R},\boldsymbol{\eta}_1-\mathbf{R},\cdots,\boldsymbol{\eta}_r-\mathbf{R})\mid n'\rangle\\&\quad\times\exp[i(\mathbf{K}'-\mathbf{K})\mathbf{R}]d\mathbf{R},\end{aligned} \tag{22}$$

where the last identity serves as a definition of an operator $G_e(\mathbf{r}_1,\cdots,\mathbf{r}_r,\mathbf{s}_1,\cdots,\mathbf{s}_r)$, acting only on electronic states, in terms of its matrix elements.

Finally we note that the atomic Hamiltonian $\bar{H}$ with the energy levels $E_{n,\mathrm{K}}$ splits into the sum

$$\bar{H}=H_\mathrm{K}+H,$$

and similarly

$$E_{n,\mathrm{K}}=E_\mathrm{K}+E_n, \tag{23}$$

where $H_\mathrm{K}$ is the Hamiltonian of the center of mass motion with energy levels

$$E_\mathrm{K}=\hbar^2\mathbf{K}^2/2M, \tag{24}$$

with $M$ the mass of the atom, and $H$ is the Hamiltonian of the relative motion of the electrons with the electronic energy levels $E_n$.

Noting (21), (22), and (23) we can now write (14) in terms of a trace over electronic states. Indeed we have

$$\begin{aligned}\bar{f}(\mathbf{x}_1,\tau_1;\cdots;\mathbf{x}_s,\tau_s;\boldsymbol{\xi}_1,\cdots,\boldsymbol{\xi}_r,\boldsymbol{\eta}_1,\cdots,\boldsymbol{\eta}_r)&=V^{-(s+1)}\int\cdots\int d\mathbf{R}d\mathbf{R}_1\cdots d\mathbf{R}_s\sum_{\mathrm{KK_1\cdots K_s}}\exp[-\sigma_0E_{\mathrm{K}_s}i\mathbf{K}(\mathbf{R}-\mathbf{R}_1)]\\&\quad\times\exp[-\sigma_1E_{\mathrm{K}_1}i\mathbf{K}_1(\mathbf{R}_1-\mathbf{R}_2)]\cdots\exp(-\sigma_sE_{\mathrm{K}_s})\exp[i\mathbf{K}_s(\mathbf{R}_s-\mathbf{R})]\\&\quad\times\mathrm{Tr}[\exp(-\beta H)\rho(\mathbf{x}_1-\mathbf{R}_1,\tau_1)\cdots\rho(\mathbf{x}_s-\mathbf{R}_s,\tau_s)G_e(\boldsymbol{\xi}_1-\mathbf{R},\cdots,\boldsymbol{\xi}_r-\mathbf{R},\boldsymbol{\eta}_1-\mathbf{R},\cdots,\boldsymbol{\eta}_r-\mathbf{R})],\end{aligned} \tag{25}$$

where

$$\sigma_0=\beta-\tau_1,\qquad\sigma_1=\tau_2-\tau_1,\cdots,\sigma_s=\tau_s, \tag{26}$$

and

$$\sigma_0+\sigma_1+\cdots+\sigma_s=\beta, \tag{27}$$

and where we have defined now

$$\rho(\mathbf{r},\tau)=\exp(\tau H)\rho(\mathbf{r})\exp(-\tau H). \tag{28}$$

[Note that (28) relates to operators acting on the states of internal motion of an atom, while (13) relates to operators acting on the full states of the atom.] The $s+1$ summations in (25) reduce in the limit of a large volume to integrals and noting (24) we have

$$\begin{aligned}V^{-1}\sum_\mathrm{K}\exp(-\sigma E_\mathrm{K}+i\mathbf{KR})&=\Lambda_\sigma^{-3}\exp[-\pi(R/\Lambda_\sigma)^2]\\&\equiv D_\sigma(\mathbf{R}),\end{aligned} \tag{29}$$

where $\Lambda_\sigma$ is a thermal wavelength

$$\Lambda_\sigma=(2\pi\hbar^2\sigma/M)^{1/2}. \tag{30}$$

It is seen from (29) that, since $\sigma\leq\beta$, one has in the limit of small $\beta$

$$D_\sigma(\mathbf{R})\sim\delta(\mathbf{R}). \tag{31}$$

Thus the $s+1$ fold sum in (25) reduces to a product of $s+1$ sharply peaked Dirac $\delta$-type functions and the main contribution to the $s+1$ fold integral over the variables $\mathbf{R},\mathbf{R}_1,\cdots,\mathbf{R}_s$, comes from a narrow domain around the line $\mathbf{R}=\mathbf{R}_1=\cdots=\mathbf{R}_s$. Hence, provided the charge density operators $\rho(\mathbf{x}_i-\mathbf{R}_i)$ included in the trace in (25) change slowly within a distance of the order of $\Lambda$, i.e., if $\Lambda$ is much smaller than the atomic dimensions, one can replace all $\mathbf{R}_i$ in the trace by $\mathbf{R}$.

Furthermore, since now the integration over $\mathbf{R}_1, \cdots, \mathbf{R}_s$ in (25) reduces to an $s$ fold convolution which can be evaluated to give

$$\int \cdots \int d\mathbf{R}_1 \cdots d\mathbf{R}_s D_{\sigma_0}(\mathbf{R}-\mathbf{R}_1) D_{\sigma_1}(\mathbf{R}_1-\mathbf{R}_2)$$
$$\times \cdots D_{\sigma_s}(\mathbf{R}_s-\mathbf{R}) = [1/(2\pi)^3]\int d\mathbf{k} \exp[-(k^2\Lambda^2/4\pi)]$$
$$=\Lambda^{-3}, \quad (32)$$

where by (27) and (30)

$$\Lambda^2 = \Lambda_{\sigma_0}{}^2 + \Lambda_{\sigma_1}{}^2 + \cdots + \Lambda_{\sigma_s}{}^2 = 2\pi\hbar^2\beta/M, \quad (33)$$

we obtain from (25), noting (29), (31), and (32)

$$\bar{f}(\mathbf{x}_1, \tau_1, \cdots, \mathbf{x}_s, \tau_s, \boldsymbol{\xi}_1, \cdots, \boldsymbol{\xi}_r, \boldsymbol{\eta}_1, \cdots, \boldsymbol{\eta}_r)$$
$$= \Lambda^{-3} \int d\mathbf{R} \int f(\mathbf{x}_1-\mathbf{R}, \tau_1, \cdots, \mathbf{x}_s-\mathbf{R}, \tau_s, \boldsymbol{\xi}_1-\mathbf{R}, \cdots, \boldsymbol{\xi}_r$$
$$-\mathbf{R}, \boldsymbol{\eta}_1-\mathbf{R}, \cdots, \boldsymbol{\eta}_r-\mathbf{R}), \quad (34)$$

where the $f$ function (without the bar) on the rhs of (34) is the intra-atomic correlation relative to the center of mass of the atom and is defined by

$$f(\mathbf{r}_1, \tau_1, \cdots, \mathbf{r}_s, \tau_s, \mathbf{p}_1, \cdots, \mathbf{p}_r, \mathbf{q}_1, \cdots, \mathbf{q}_r)$$
$$= \mathrm{Tr}[\exp(-\beta H) \rho(\mathbf{r}_1, \tau_1) \cdots \rho(\mathbf{r}_s, \tau_s)$$
$$\times G_e(\mathbf{p}_1, \cdots, \mathbf{p}_r, \mathbf{q}_1, \cdots, \mathbf{q}_r)]. \quad (35)$$

This result shows that in the limit of classical nuclear motion the diagrammatic formulation of the expansion of log $\Xi$ and of the $b_l$'s can be preserved as before and that moreover the big circles with their connection points appearing in a diagram can be interpreted in terms of the full intraatomic correlation functions on the lhs of (34) or in terms of intraatomic correlation functions relative to the center of mass of the atom given on the rhs of (35). Furthermore since the big circles in a diagram imply integration over the positions of the centers of mass of the atoms, the same diagram with fixed position assigned to each big circle can equally represent the integrand. Thus the sum of all connected diagrams having $l$ big circles with fixed assigned coordinates (fixed big circles) is a valid representation of the expansion of the function of $l$ nuclear coordinates whose integral gives $Vb_l$. More specifically, the sum of all connected diagrams having fixed $l$ big circles is equal to $b_1{}^l U_l(\mathbf{R}_1, \cdots, \mathbf{R}_l)$. In particular for $l=2$, $f(R) = b_1{}^{-2}$ times the sum of all connected diagrams with two fixed big circles.

## IV. PERTURBATION EXPANSION OF $f(R)$

In the case of two atoms only, the diagrammatic formulation of the perturbation expansion has no significant advantage over the following compact way of writing the expansion. The interaction energy operator between the two atoms is given according to (11) by

$$\bar{V} = \int\int [\bar{\rho}_a(\mathbf{x}) \bar{\rho}_b(\mathbf{y}) / |\mathbf{x}-\mathbf{y}|] d\mathbf{x} d\mathbf{y}, \quad (36)$$

where the indices $a$, $b$ refer to two distinct atoms. In the classical limit for nuclear motion this leads to an interaction

$$V = \int\int [\rho_a(\mathbf{x}-\mathbf{R}_1) \rho_b(\mathbf{y}-\mathbf{R}_2) / |\mathbf{x}-\mathbf{y}|] d\mathbf{x} d\mathbf{y}, \quad (37)$$

between the two atoms at fixed positions $R_1$, $R_2$ of their nuclei. In addition we require to define the transformed operator

$$V(\tau) = \exp(\tau H_0) V \exp(-\tau H_0), \quad (38)$$

where

$$H_0 = H_a + H_b. \quad (39)$$

Comparing (37) and (38) with (28) we obviously have

$$V(\tau) = \int\int [\rho_a(\mathbf{x}-\mathbf{R}_1, \tau) \rho_b(\mathbf{y}-\mathbf{R}_2, \tau) / |\mathbf{x}-\mathbf{y}|] d\mathbf{x} d\mathbf{y}. \quad (40)$$

We can now write

$$f(R) = b_1{}^{-2}\Lambda^{-6}[\sum_{s=0} [(-1)^s/s!] \mathrm{Tr}\{\exp(-\beta H_0)$$
$$\times T[V(\tau_1) \cdots V(\tau_2)] A\} d\tau_1 \cdots d\tau_s - \mathrm{Tr} \exp(-\beta H_0)], \quad (41)$$

where $\mathbf{R} = \mathbf{R}_1 - \mathbf{R}_2$, the trace is taken in terms of the internal states of the two independent fixed atoms and $A$ is an antisymmetrizing operator with respect to interchange of electrons between the two atoms. A formal summation of (41) yields

$$f(R) = b_1{}^{-2}\Lambda^{-6}\{\mathrm{Tr}[\exp(-\beta H) A] - \mathrm{Tr} \exp(-\beta H_0)\}, \quad (42)$$

with

$$H = H_0 + V, \quad (43)$$

and this is the necessary limiting classical form obtained from (1). Denoting by $|n_a, n_b)$ the eigenstates of $H_0$, where $n_a$, $n_b$ are the quantum numbers of the internal states of atom $a$ and atom $b$, we can write for (42)

$$f(R) = b_1{}^{-2}\Lambda^{-6} \sum_{n_a, n_b} (n_a, n_b | \exp(-\beta H) A$$
$$-\exp(-\beta H_0) | n_a, n_b). \quad (44)$$

In the following we shall also make use of the shorthand notation

$$|n_a, n_b) \equiv |n), \qquad E_{n_a} + E_{n_b} \equiv E_n,$$

for the eigenstates and eigenvalues of $H_0$, respectively.

Being interested in stable molecular gases, we shall consider only temperatures sufficiently low so that $kT$ is small compared to the internal excitation energy of the atom, i.e., we shall assume that

$$\beta(E_n - E_0) \gg 1, \qquad |n) \neq |0, 0), \quad (45)$$

where $|0) \equiv |0, 0)$ is the ground state of the pair of atoms. Hence the upper electronic states do not contribute to the trace in (42) and (41), i.e., instead of

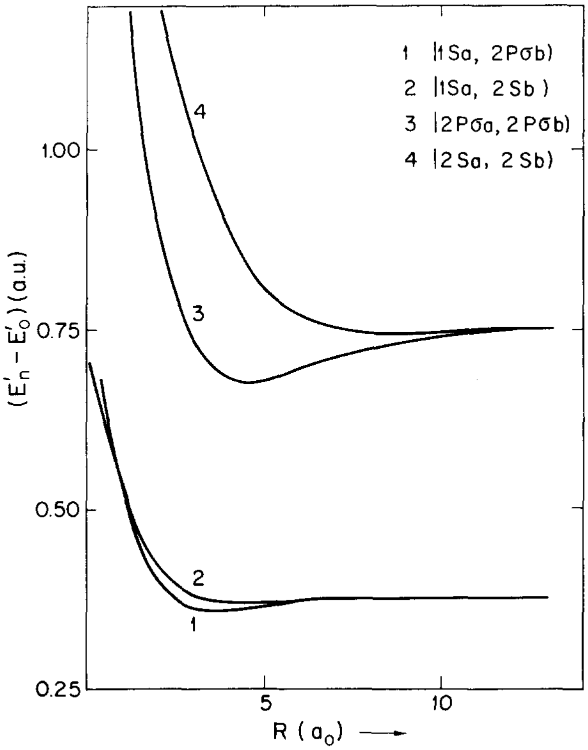

FIG. 2. Excitation energies, modified by static Coulomb interaction, for four states excited from the ground state $|0) \equiv |1Sa, 1Sb)$, as a function of $R$.

(44) we have

$$f(R)=b_1^{-2}\Lambda^{-6}[(0\mid \exp(-\beta H)A\mid 0)-\exp(-\beta E_0)]. \tag{46}$$

Note that this assumption is weaker than the assumption leading from (4) to (3) since the latter implies that for all $R$ the electronically excited states are high above the ground state, while the former requires only that it holds for $R=\infty$.

Comparing (46) with (41) and (42) and noting that by our preceding assumption about the classical limit we must have

$$b_1=\Lambda^{-3}\exp(-\beta E_{0_a}), \tag{47}$$

it follows from (41) that

$$1+f(R)=\sum_{s=0}^{\infty}\frac{(-1)^s}{s!}\times\int\cdots\int(0\mid T[V(\tau_1)\cdots V(\tau_s)]A\mid 0)d\tau_1\cdots d\tau_s, \tag{48}$$

and this can serve as a perturbation expansion of $f(R)$.

A serious drawback of (48) is its slow convergence when $R$ is small, which follows from the fact that the diagonal matrix elements of $V(\tau)$ or $V$ include, noting (37), (18), and (20), a nuclear Coulomb repulsion term $e^2Z^2/R$ which diverges for $R\rightarrow 0$ and causes each term of (48) to diverge in this limit. This divergence can be overcome by decomposing $V$ into a sum of a finite part and a diagonal divergent part. Then a resummation of (48) can be achieved which leads to a term by term finite expansion as $R\rightarrow\infty$. The decomposition is not unique. Indeed in the last section we consider a decomposition which, though approximate, leads to an expression for $f(R)$ having some desirable properties to be discussed there. Here we have chosen to split $V$ into

$$V=V^0+V', \tag{49}$$

where

$$V^0=\sum_n \mid n)(n\mid V\mid n)(n\mid, \tag{50}$$

is diagonal and

$$V'=\sum_{n\neq m}\mid n)(n\mid V\mid m)(m\mid, \tag{51}$$

which has zero diagonal elements but whose nondiagonal elements coincide with those of $V$.

We shall skip here over the resummation procedure and derive the resulting expansion more directly. Writing

$$H=H_0'+V', \tag{52}$$

where

$$H_0'=H_0+V^0, \tag{53}$$

and denoting corresponding eigenvalue of $H_0'$ by $E_n'$ (the eigenstates coincide with those of $H_0$), we make a new Dyson expansion of $e^{-\beta H}$ with respect to the perturbation $V'$. Substituting this into (46) and noting (47) we obtain our resummed expansion

$$1+f(R)=\exp[-\beta(0\mid V\mid 0)]\sum_{s=0}^{\infty}\frac{(-1)^s}{s!}\times\int\cdots\int(0\mid T[V'(\tau_1)\cdots V'(\tau_s)]A\mid 0)\times d\tau_1\cdots d\tau_s, \tag{54}$$

where now

$$V'(\tau)=\exp(\tau H_0')V'\exp(-\tau H_0'). \tag{55}$$

We see from here that the divergent Coulomb repulsion of the nuclei appears only in the exponent in front of the sum in (54) and that consequently $1+f(R)$ quickly approaches zero when $R$ becomes small.

In order to make a specific evaluation of the low order terms of (53), we have to consider the eigenvalues $E_n'$ of $H_0'$. Denoting

$$V_{mn}=(m\mid V\mid n), \tag{56}$$

we can write for these

$$E_n'=E_n+V_{nn}. \tag{57}$$

The $E_n'$ represent "Coulomb interaction" curves (functions of $R$), shifted by the amount $E_n$. Our following method of evaluating terms in (54) depends on the validity of the inequality

$$\beta(E_n'-E_0')\gg 1, \qquad |\,n)\neq|\,0,0), \tag{58}$$

analogous to our assumption (45) on the electronic excitation energies which led to (46). That indeed (58) holds for all $R$ can be demonstrated for a simplified atomic model which we shall apply in all following specific calculations. For this atomic model it is assumed on the one hand that the atom consists of a single electron and a structureless ionic core, and on the other hand that the electron is part of a closed shell and thus it cannot be exchanged with an electron from another atom having opposite spin. More simply we assume that the atoms are all hydrogen like and have all electrons with parallel spins. Thus throughout our numerical calculations we shall use hydrogen wavefunctions to represent internal atomic states. The difference $E_n'-E_0'$ for 4 excited states $|\,n)$ of such a pair of atoms are plotted in Fig. 2 which indicates that the assumption (58) does indeed hold.

Noting that for our atomic model we have

$$A=1-P, \tag{59}$$

where $P$ is an exchange operator of coordinates of an electron pair, one can now write the zero, first and second order terms in (54) as follows

$$1+f(R)=\exp(-\beta V_{00})\Big\{1-(0\,|\,P\,|\,0)$$

$$-\int_0^\beta\sum_{n=0}^{\infty}V_{0n}'(\tau)d\tau(n\,|\,1-P\,|\,0)+\frac{1}{2}\int_0^\beta\int_0^\beta d\tau_1 d\tau_2$$

$$\times T[\sum_{mn}V_{0n}'(\tau_1)V_{nm}'(\tau_2)](m\,|\,1-P\,|\,0)\Big\}. \tag{60}$$

Once (58) is assumed, the evaluation of the integrals in (60) is a standard procedure, since it enables to replace one integration limit $\beta$ in each integral by infinity. Observing that $V'$ has zero diagonal elements we obtain

$$1+f(R)=\exp(-\beta V_{00})(1-S^2+B'+\beta C'-D'), \tag{61}$$

where

$$S^2=(0\,|\,P\,|\,0),$$

$$B'=\sum_{n\neq 0}(V_{0n}/E_{0n}')(n\,|\,P\,|\,0),$$

$$C'=\sum_{n\neq 0}(|\,V_{0n}\,|^2/E_{0n}')(1-S^2),$$

$$D'=\sum_{n\neq m\neq 0}(V_{0n}V_{nm}/E_{0n}'E_{0m}')(m\,|\,P\,|\,0), \tag{62}$$

and where, noting (57), the denominator $E_{0n}'$ in (62) is given by

$$E_{0n}'=E_n'-E_0'=E_{0n}+V_{nn}-V_{00},$$

$$E_{0n}=E_n-E_0. \tag{63}$$

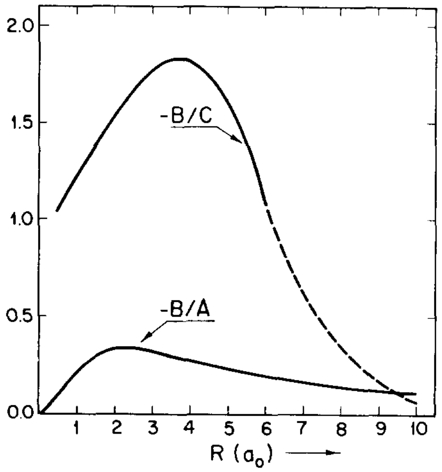

FIG. 3. Ratios of $B$, $C$ [Eq. (64)] and $A\equiv S^2$ as functions of R.

$B'$ has been obtained by performing the integration in the single integral on the rhs of (60). Similarly $\beta C'$ and $D'$ are, respectively, the $\beta$ proportional term and the $\beta$-independent term obtained by performing the integration in the double integral on the rhs of (60).

## V. ESTIMATE OF MAGNITUDE OF TERMS

We now shall make an order of magnitude estimate of the various terms on the rhs of (61). For this purpose we introduce an Unsöld type approximation[5] of replacing the denominators in two expressions in (62) by an average "ionization potential" $I(R)$, which depends on $R$ because of the static Coulomb interactions included in $E_{0n}'$. This enables us to carry out the summations in (62) which we write as

$$B=\sum_{n\neq 0}V_{0n}(n\,|\,P\,|\,0)=(0\,|\,VP\,|\,0)-V_{00}S^2,$$

$$C=\sum_{n\neq 0}|\,V_{0n}\,|^2(1-S^2)=[(0\,|\,V^2\,|\,0)-V_{00}{}^2](1-S^2), \tag{64}$$

and we obtain

$$B'\approx B/I(R), \qquad C'\approx C/I(R). \tag{65}$$

The method of computing $B$ and $C$ is summarized in the appendix.[6] In Fig. 3 the ratio $B/C$ is shown diagrammatically as a function of $R$. From there, it is seen that $|\,B\,|$ is for all $R$ at most of the order of magnitude of $C$. To compare $B'$ with $\beta C'$ we choose $\beta\sim 10^2$ a.u.$^{-1}$, a value which conforms to the condition (58) since excitation energies $E_{0n}'$, as well as $I(R)$, are of the order of 1 a.u. for $R>1a_0$. Hence $B'$ is always small compared to $\beta C'$. We assume that in a similar fashion

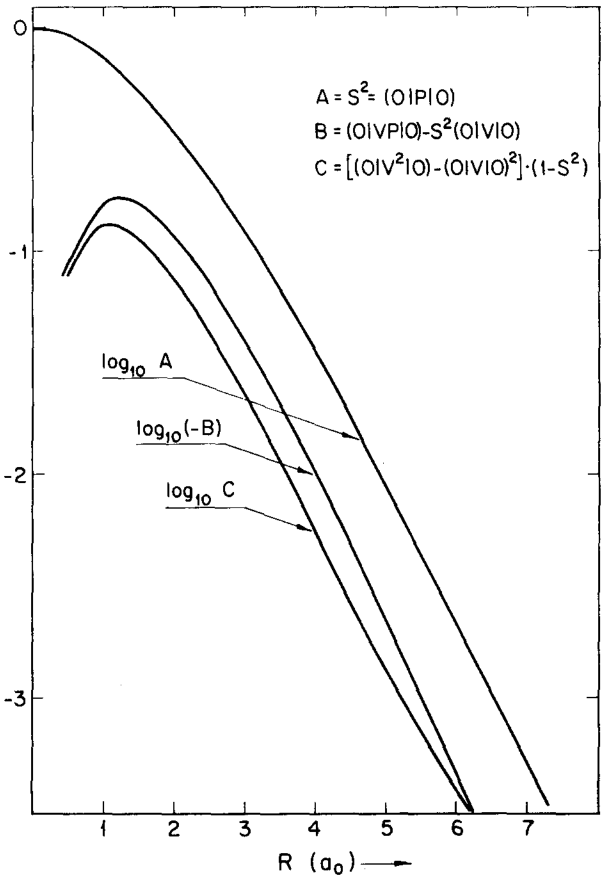

FIG. 4. Plot of $A=S^2$, $B$, and $C$ [Eq. (64)] as functions of $R$.

one could compare the term $D'$ to that part of the third order terms which is proportional to $\beta$ and find that for our chosen range of $\beta$, $D'$ is small compared to such third order terms. Consequently, we have considered only the 3 terms $S^2$, $B'$ and $C'$ in (61). They all are strongly dependent on $R$ and we have plotted the ratio of the 3 functions $S^2$, $B$ and $C$ in Fig. 3 and their absolute values on a logarithmic scale in Fig. 4.

The strong dependence on $R$ requires a separate consideration of long, medium, and short range values of $R$. Reexamining the terms in (61), given by (62), one can observe the following. The factors $S^2=(0\mid P\mid 0)$ and $(n\mid P\mid 0)$, which are overlap integrals of ground and excited state atoms and which appear in (61) as a consequence of electron exchange, must decay exponentially with increasing $R$. Thus for large $R$ values only the exchange independent part of the second order term $\beta C'$ remains. Moreover for such $R$, $E_{0n}'$ can be replaced by $E_{0n}$, since they differ (see (63)] by static Coulomb interactions of the two atoms and these terms also decay exponentially with $R$. Hence $C'$ reduces to minus the van der Waals interaction energy of the atoms. Writing thus

$$-C'=u(R), \qquad (66)$$

and noting that $\beta u(R)\ll 1$, we obtain from (61), to the same order of approximation

$$1+f(R)=1+\beta C'=\exp[-\beta u(R)]. \qquad (67)$$

At shorter distances $R$, the exchange integrals cannot be neglected and the contribution of all terms on the rhs of (61) to $f(R)$ must be considered. Noting the plots in Fig. 4 we shall however restrict ourselves to sufficiently large $R$ values so that the largest term in (61), namely $\beta C'$, is less than 1/2. For our chosen range of temperatures, given by $\beta\sim 10^2$ a.u.$^{-1}$, this amounts to $R$ values larger than $4a_0$ and this shall define our medium range of $R$ values. As mentioned above $B'$ can always be neglected in comparison to $\beta C'$ for our chosen values of $\beta$. Similarly also $S^2$ can be neglected in comparison to $\beta C'$ for our chosen $\beta$ and $R$ values. Hence for medium range $R$'s we can write

$$V_{00}-C'=u(R), \qquad (68)$$

and have to the same order of approximation

$$1+f(R)=\exp(-\beta V_{00})(1+\beta C')=\exp[-\beta u(R)]. \quad (69)$$

Thus it seems that for the medium range of $R$'s for which (69) holds, a potential as in (68) is defined which takes into account slight effects of electron exchange and of interpenetration of the electronic clouds. The first effect is manifest in the factor $1-S^2$ included in $C'$, whereas the second is exhibited in the shift in the energy levels from $E_n$ to $E_n'$ as well as the finite contribution $V_{00}$ to the potential.

For smaller $R$ values, and for our chosen $\beta$, there is at least a broad intermediate range where $\beta C'$ is greater

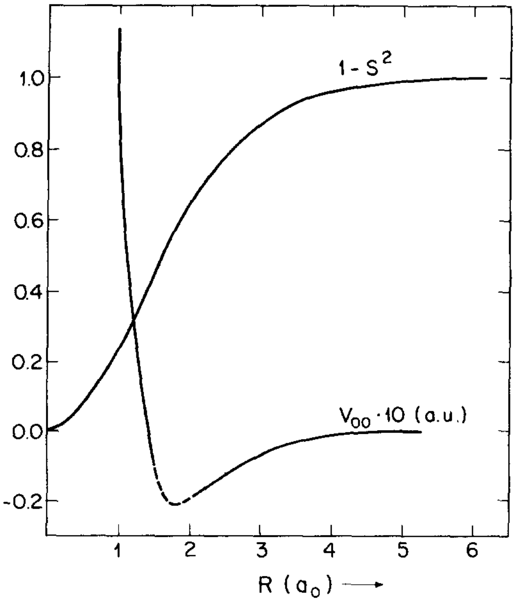

FIG. 5. Comparative plot of static Coulomb interaction energy and pure exchange terms as functions of $R$.

than unity, which indicates that for this range our truncated expansion is valid no more. One of its serious drawbacks concerns a certain range of $R$ values around $R\sim a_0$ where $V_{00}$ has a negative and minimum value (see Fig. 5) sufficiently deep to make the exponential in (61), and hence $f(R)$, positive and large compared to unity (Fig. 6). This however is not possible for a pair of hydrogen atoms in the triplet state which, as we know,[5] do repel each other at all $R$ values.

## VI. ALTERNATIVE EXPANSION OF $f(R)$

As mentioned above, the decomposition (52) on which our expansion of $f(R)$ is based, is not unique. In fact we wish to indicate an alternative expansion of $f(R)$ which is based on an approximate decomposition of the type of (52).

Following Salem,[7] we choose the set of symmetrized (unnormalized) state vectors of the pair of atoms

$$|n\rangle=A\,|n), \tag{70}$$

as an approximately orthogonal and complete basis set, although the set is in fact not exactly orthogonal and even overcomplete. The normalization factor for the vector $|n\rangle$ is $\langle n\,|\,n\rangle^{-1/2}$, where

$$\langle n\,|\,n\rangle=(n\,|\,A^2\,|\,n)=N(n\,|\,A\,|\,n), \tag{71}$$

and where $N$ is the number of permutations of electrons between the two atoms. If $p$ and $q$ are, respectively, the number of electrons in atom $a$ and $b$, then

$$N=(p+q)\,!/p\,!q\,!. \tag{72}$$

The assumption made above can be expressed in form of an approximate decomposition of the unity operator

$$1=\sum_n |\,n\rangle\langle n\,|/\langle n\,|\,n\rangle. \tag{73}$$

Accordingly we can write approximately

$$\begin{aligned}\mathrm{Tr}\exp(-\beta H)&=\sum_n \langle n\,|\exp(-\beta H)\,|\,n\rangle/\langle n\,|\,n\rangle\\&=\sum_n (n\,|\exp(-\beta H)A\,|\,n)/(n\,|\,A\,|\,n),\end{aligned} \tag{74}$$

where the last equality in (74) follows from the commutability of $A$ with $H$. Furthermore, using (73) we define an approximate decomposition of $H$

$$H=H_0'+V', \tag{75}$$

as follows

$$H_0'=\sum_n |\,n\rangle(\langle n\,|\,H\,|\,n\rangle/\langle n\,|\,n\rangle^2)\,\langle n\,|, \tag{76}$$

and

$$V'=\sum_{n\neq m} |\,n\rangle\langle n\,|\,H\,|\,m\rangle\,|\,m\,|/\langle n\,|\,n\rangle\langle m\,|\,m\rangle. \tag{77}$$

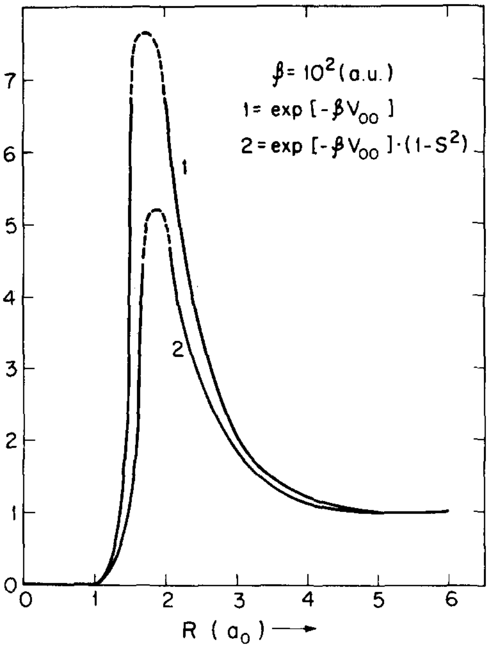

FIG. 6. Contribution of static Coulomb interaction and pure exchange to $f(R)$.

Substituting (70) and (43) into (76) we obtain for the eigenstates of $H_0'$

$$\begin{aligned}E_n'&=\langle n\,|\,H\,|\,n\rangle/\langle n\,|\,n\rangle\\&=E_n+(n\,|\,VA\,|\,n)/(n\,|\,A\,|\,n).\end{aligned} \tag{78}$$

Assuming again, as in (58), that

$$\beta(E_n'-E_0')\gg 1, \tag{79}$$

we can omit also in (74) all but the ground state term. Proceeding then with a Dyson expansion of $\exp(-\beta H)$ corresponding to the decomposition (75) we obtain from (74), in a manner analogous to (48) and (54), and noting also that from (78)

$$\begin{aligned}\langle 0\,|\exp(-\beta H_0')\,|\,0\rangle&=\exp(-\beta E_0)\\&\quad\times\exp[-\beta(n\,|\,VA\,|\,n)/(n\,|\,A\,|\,n)],\end{aligned} \tag{80}$$

the expansion

$$\begin{aligned}1+f(R)&=\exp\left(-\beta\frac{(n\,|\,AV\,|\,n)}{(n\,|\,A\,|\,n)}\right)\sum_{s=0}(-1)^s\\&\quad\times\int_{\tau_1>\cdots>\tau_s}\cdots\int\langle 0\,|\,V'(\tau_1)\cdots V'(\tau_s)\,|\,0\rangle\\&\quad\times d\tau_1\cdots d\tau_s.\end{aligned} \tag{81}$$

The striking feature of this expansion is that it results in a zero order term of the form

$$1+f(R)=\exp[-\beta u(R)], \tag{82}$$

where

$$u(R)=(0\,|\,VA\,|\,0)/(0\,|\,A\,|\,0), \tag{83}$$

is precisely the Heitler–London interaction energy,[5] and has for all $R$ the desired property of being a repulsive potential energy. Furthermore, (82) is also correct up to first order in our scheme since the first order term in (81) vanishes because of the vanishing of the diagonal elements in $V'$. [Note in contrast the appearance of a first order exchange term in (60) and (61), where the exchange operation has not been included in the definition of $H_0'$ and $V'$.] Finally, adding the second term we obtain

$$1+f(R)=\exp[-\beta(0\mid VA\mid 0)/(0\mid A\mid 0)]\times[1+\beta\sum_{n\neq 0}(\langle 0\mid H\mid n\rangle\langle n\mid H\mid 0\rangle/E_n'-E_0')\times\langle 0\mid 0\rangle^{-1}\langle n\mid n\rangle^{-1}], \quad (84)$$

and as long as the second order term in (84) is small compared to 1, we have again (82) with $u(R)$ now defined by

$$u(R)=(0\mid VA\mid 0)/(0\mid A\mid 0)-\sum_{n\neq 0}(\langle 0\mid H\mid n\rangle\langle n\mid H\mid 0\rangle/E_n'-E_0')\langle 0\mid 0\rangle^{-1}\langle n\mid n\rangle^{-1}. \quad (85)$$

This potential includes now in addition to the Heitler–London first order exchange term also the second order van der Waals interaction energy with additional exchange terms implied in the matrix elements $\langle 0\mid H\mid n\rangle$. For long range $R$ values the first order interaction and exchange contributions can be neglected and we are left in (85) with the van der Waals interaction energy.

## VII. CONCLUSION

The two particular expansions of $f(R)$ considered presently have proved to be of limited validity at short distances $R$. The method of Sec. 6 is by the assumption (73) limited to the case of slight or no overlap of the wavefunctions of the two atoms. On the other hand the expansion developed in Secs. 4 and 5 is based only on the assumption that $f(R)$ can be expressed as a functional of states of the two isolated molecules. Therefore it is hoped that there does exist a method of resummation of (54) and of collecting of terms which yields a more efficient expansion of $f(R)$ valid also for small $R$.

## APPENDIX

The evaluation of $B$ and $C$ [Eq. (64)] was performed as follows. Writing the Coulomb interaction energy of two hydrogen atoms in the form

$$V=R^{-1}+r_{12}^{-1}-r_{2a}^{-1}-r_{1b}^{-1}, \quad (A1)$$

we have, utilizing symmetry of terms,

$$B=(0\mid VP\mid 0)-(0\mid V\mid 0)S^2=(0\mid r_{12}^{-1}P\mid 0)-S^2(0\mid r_{12}^{-1}\mid 0)-2[(0\mid r_{a2}^{-1}P\mid 0)-S^2(0\mid r_{a2}^{-1}\mid 0)], \quad (A2)$$

and

$$\bar{C}=(0\mid V^2\mid 0)-\mid(0\mid V\mid 0)\mid^2=(0\mid 1/r_{12}^2\mid 0)-(0\mid r_{12}^{-1}\mid 0)\mid^2+2[(0\mid 1/r_{a2}^2\mid 0)-\mid(0\mid r_{a2}^{-1}\mid 0)]^2-4[(0\mid 1/r_{12}r_{a2}\mid 0)-(0\mid 1/r_{12}\mid 0)(0\mid 1/r_{a2}\mid 0)], \quad (A3)$$

where the ground state of the two atoms is $\mid 0)=\mid 1s_a, 1s_b)$. All the necessary matrix elements can be found among the evaluated integrals listed by Eisenschitz and London[8] in their appendix. Using their numbering of integrals we write

$$B=R(I_{14}-S^2I_4)-2R(I_{13}-S^2I_3),$$
$$\bar{C}=I_5-R^2I_4+2(I_{11}-R^2I_3^2)-4(I_7-R^2I_3I_4), \quad (A4)$$

and a straightforward numerical evaluation then follows.

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[1] R. W. Zwanzig, Phys. Rev. **106**, 13 (1957).

[2] See, e.g., G. E. Uhlenbeck and G. W. Ford, *Studies in Statistical Mechanics* (North-Holland, Amsterdam, 1962), Vol. 1, Pt. B.

[3] B. Linder, Discussions Faraday Soc. **40**, 164 (1965); Advan. Chem. Phys. **12**, 225 (1967).

[4] S. Baer, J. Chem. Phys. **49**, 3632 (1968); **47**, 2889 (1967).

[5] See, e.g., H. Margenau and N. R. Kestner, *Theory of Intermolecular Forces* (Pergamon, New York, 1969).

[6] Throughout atomic units (a.u.) are used to represent numerical results. Thus the unit of length is $a_0$= Bohr radius = 0.53 Å and the unit of energy is $e^2/a_0=2$ Ry. = 27.21 eV. The reciprocal temperature $\beta$ is then given in reciprocal energy atomic units (a.u.$^{-1}$) so that $\beta=10^2$ a.u.$^{-1}$ say, is equivalent to $T\sim 3000$°K.

[7] L. Salem, Discussions Faraday Soc. **40**, 150 (1965).

[8] R. Eisenschitz and F. London, Z. Physik **60**, 491 (1930).