# EXCHANGE EFFECTS IN QUANTUM STATISTICAL MECHANICS

by

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Under the supervision of
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A combinatorial treatment of exchange effects for many-particle systems is made by writing the N-particle cluster integral for a system of hard-sphere bosons in three dimensions as a weighted sum of cyclic-exchange cluster integrals. The relative size of each exchange term is then systematically evaluated and its behavior numerically simulated as a function of temperature, density, and particle number.

A comment is made on the formal procedure for treating composite particle statistics. Limitations are discussed on composite particles that can be treated as bosons.

The ground state of the molecular trimer is studied in three dimensions for four potential models: the square-well, the exponential, the yukawa, and the gaussian. The exchange symmetries for the boson trimer and for the spin-1/2 and spin-3/2 fermion trimers are treated and incorporated into the trial wavefunctions for these three cases.

This distinguishes the energies of these cases. Bounds of the threshold binding parameters are numerically calculated in each case and compared to two-body parameters.

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# INTRODUCTION

The quantum-mechanical principle of indistinguishability of identical particles is often interpreted with the idea that due to the overlapping of the individual particle wavefunctions,it is impossible to tell which function is due to which particle.

The principle of indistinguishability combined with the spin-statistics of the particles leads to exchange effects in observed quantities.

There are many examples of exchange effects in physics and chemistry. In nuclei, exchange effects of mesons lead to internuclear forces. On the atomic scale, the Pauli exclusion principle leads to the electron shell structure. Between atoms, short range interactions have repulsions due to distortions of atomic electron distributions. In metals, exchange interactions affect the electron distributions. The Heisenberg spin interaction between neighboring atoms in a ferromagnetic lattice is due to atomic overlap. Nuclei spin-statistics appear in the rotational spectra of diatomic molecules, both in molecular spectroscopy and in the specific heat of the gas. In liquid $^3$He and $^4$He, the different phases have different exchange structures. The superfluid phase of

$^4$He suggest that to a large extent, $^4$He atoms can be treated as bosons.

We believe that exchange effects are also important between more massive objects like molecules, where the intermolecular forces are much weaker than those binding the molecules together. Here we regard the molecule as a composite boson or fermion. We consider some of the ways that exchange considerations affect the existence of molecular associates like the trimer.

This thesis is divided into two parts. Part I deals with exchange effects in a many particle system. Part II treats the exchange effects in the three-body problem.

We take the position that the wavefunction, even a trial wavefunction in a variational calculation, should carry the knowable information in the form of quantum numbers of the system.

There are two spin cases for a trimer composed of spin-1/2 fermions: the total spin can be 1/2 or 3/2. The exchange symmetries of these two fermion cases are different from each other and from the boson case. These different exchange symmetries lead to different forms of variational trial wavefunctions which lead to different variational energies for the three cases. From this we conclude that even on this relatively large scale, quantum indistinguishability is important as it may in certain cases restrict the formation of some of these molecular trimers.

# PART I

# MANY-BODY EXCHANGE EFFECTS

# CHAPTER 1

# EXCHANGE CLUSTER INTEGRALS FOR HARD SPHERES

Exchange effects resulting from quantum statistics of identical particles enter into quantum expressions for the partition function, correlation function, and virial coefficients of a many particle system. The behavior of these exchange terms is believed to be related to observable properties, e.g., the λ-transition in Helium.

Analysis of these terms is complicated by the enormous numbers of possible exchanges. For example, there are $2.6313 \times 10^{35}$ permutations of only thirty two particles. To have any chance of following the behavior of exchange terms, it is necessary to simplify and systematize the approach used, so that only the more important exchanges can be given a more detailed treatment.

A permutation of N particles can be written as a product of cyclic exchanges on subsets of the particles. When the interactions of the particles are over a short range, and when the thermal wavelength is small in comparison to $1/\rho^{1/3}$, the particles can be thought of as being essentially free much of the time; an approximation can be made and a combinational treatment can be adopted from the ideal Bose gas, in which the symmetrized N-particle cluster integral for a system of bosons[1] is written as a weighted sum of cyclic-exchange cluster integrals. The relative size of each exchange term is then systematically evaluated and its behavior numerically simulated as a function of temperature, density, and particle number.

It is noted that the models presented here are in three dimensions.

## A. Formulation

The cluster integrals are written as integrals of the N-body thermodynamic Green's function

$$G_{3N}(\underset{\sim}{r}_1'\ldots\underset{\sim}{r}_N';\underset{\sim}{r}_1\ldots\underset{\sim}{r}_N;\beta) = \langle\underset{\sim}{r}_1'\ldots\underset{\sim}{r}_N'|\exp(-\beta H_N)|\underset{\sim}{r}_1\ldots\underset{\sim}{r}_N\rangle \tag{1.1}$$

which solves the N-dimensional Bloch equation

$$(H_N + \frac{\partial}{\partial\beta})G_{3N} = 0 \tag{1.2}$$

with the initial condition

$$G_{3N}(\underset{\sim}{r}_1'\ldots\underset{\sim}{r}_N';\underset{\sim}{r}_1\ldots\underset{\sim}{r}_N;0) = \prod_{i=1}^{N} \delta^3(\underset{\sim}{r}_i'-\underset{\sim}{r}_i) \tag{1.3}$$

and the boundary condition

$$G_{3N}\to 0 \text{ as } |\underset{\sim}{r}_i'-\underset{\sim}{r}_i| \to \infty \tag{1.4}$$

$G_{3N}$ has a functional integral expression

$$<\underset{\sim}{r}_1'\cdots\underset{\sim}{r}_N'|\exp(-\beta H_N)|\underset{\sim}{r}_1\cdots\underset{\sim}{r}_N> \; = \int_{\underset{\sim}{r}_1}^{\underset{\sim}{r}_1'}\cdots\int_{\underset{\sim}{r}_N}^{\underset{\sim}{r}_N'} \mathcal{D}X_1(t)\cdots\mathcal{D}X_N(t)\exp\left(\frac{-S[\underset{\sim}{X}_1(t)\cdots\underset{\sim}{X}_N(t)]}{\hbar}\right) \tag{1.5}$$

where the action

$$S[\underset{\sim}{X}_1(t)\cdots\underset{\sim}{X}_N(t)]=\int_0^{\beta\hbar} dt\{\tfrac{1}{2}M\,\dot{X}_1^2(t)+\cdots+\tfrac{1}{2}M\,\dot{X}_N^2(t)+V[\underset{\sim}{X}_1(t)\ldots\underset{\sim}{X}_N(t)]\}, \tag{1.6}$$

The cyclic exchange cluster integral[2] is the N-particle volume integral of the thermodynamic Green's function where the final N-particle positions are a cyclic permutation of the initial positions:

$$b_N(\text{cycle})=\frac{1}{N!\Omega}\int_\Omega\cdots\int_\Omega d\underset{\sim}{r}_1\cdots d\underset{\sim}{r}_N<\underset{\sim}{r}_2\cdots\underset{\sim}{r}_N\underset{\sim}{r}_1|\exp(-\beta H_N)|\underset{\sim}{r}_1\cdots\underset{\sim}{r}_N>. \tag{1.7}$$

The symmetrized N-particle cluster integral for a system of bosons:[1]

$$b_N^S(\Omega)=\frac{1}{N!\Omega}\sum_{\text{permutation}}\int_\Omega\cdots\int_\Omega d\underset{\sim}{r}_1\cdots d\underset{\sim}{r}_N<\underset{\sim}{r}_1'\cdots\underset{\sim}{r}_N'| \times \exp(-\beta H_N)|\underset{\sim}{r}_1\cdots\underset{\sim}{r}_N> \tag{1.8}$$

where the sum is over the N! permutations of the N-particles. The $\underset{\sim}{r}_1'\cdots\underset{\sim}{r}_N'$ are permutations of the $\underset{\sim}{r}_1\cdots\underset{\sim}{r}_N$.

## B. Ideal Bose Gas

For a non-interacting Bose gas,

$$H_N = \sum_{i=1}^{N} \frac{p_i^2}{2M}$$

$$G_{3N}(\underset{\sim}{r}_1'\ldots\underset{\sim}{r}_N';r_1\ldots r_N;\beta) = \langle\underset{\sim}{r}_1'\ldots\underset{\sim}{r}_N'|\exp(-\beta\sum_{i=1}^{N}\frac{p_i^2}{2M})|\underset{\sim}{r}_1\ldots\underset{\sim}{r}_N\rangle$$

$$= \frac{1}{\lambda^{3N}}\exp[-\frac{\pi}{\lambda^2}\sum_{i=1}^{N}(\underset{\sim}{r}_i'-\underset{\sim}{r}_i)^2] \qquad (1.9)$$

where λ is the thermal wavelength

$$\lambda \equiv [\frac{2\pi\beta\hbar^2}{M}]^{\frac{1}{2}} \qquad (1.10)$$

$$b_N(\text{cycle})=\frac{1}{N!\Omega}\int_\Omega\ldots\int_\Omega d\underset{\sim}{r}_1\ldots d\underset{\sim}{r}_N\langle\underset{\sim}{r}_2\ldots\underset{\sim}{r}_N\underset{\sim}{r}_1|$$

$$\times\ \exp(-\beta\sum_{i=1}^{N}\frac{p_i^2}{2M})|\underset{\sim}{r}_1\ldots\underset{\sim}{r}_N\rangle \qquad (1.11)$$

$$= \frac{1}{N!\Omega}\int_\Omega\ldots\int_\Omega d\underset{\sim}{r}_1\ldots d\underset{\sim}{r}_N\frac{1}{\lambda^{3N}}\exp[-\frac{\pi}{\lambda^2}\sum_{i=1}^{N}(\underset{\sim}{r}_i-\underset{\sim}{r}_{i-1})^2]$$

with $\underset{\sim}{r}_o\equiv\underset{\sim}{r}_N$.

$$b_N(\text{cycle}) = \frac{1}{N!\Omega}\int_\Omega d\underset{\sim}{r}_N\frac{1}{\lambda^{3N}}\frac{\lambda^{3(N-1)}}{N^{3/2}}$$

$$= \frac{1}{N!\ \lambda^3\ N^{3/2}} \qquad (1.12)$$

The symmetrized cluster integral can be calculated from (1.8) by decomposing each permutation into $n_\ell$ $\ell$-cycle exchanges, where

$$N = \sum_{\ell=1}^{N} \ell n_\ell \tag{1.13}$$

there are $\dfrac{N!}{\prod_{\ell=1}^{N} \ell^{n_\ell}\, n_\ell!}$ permutations of each type characterized by a set $\{n_\ell\}_{\ell=1}^{N}$.[3] For non-interacting particles the Green's function factors and only the cyclic exchange terms contribute.

$$b_N^S(\Omega) = \frac{1}{\Omega} \sum_{\{n_\ell\}} \int\cdots\int d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N \prod_{\ell=1}^{N} \frac{1}{\ell^{n_\ell}\, n_\ell!}\, \Omega^{n_\ell}$$

$$\times \left(\frac{1}{\Omega} \langle \underset{\sim}{r}_2 \cdots \underset{\sim}{r}_\ell \underset{\sim}{r}_1 | \exp(-\beta H_\ell) | \underset{\sim}{r}_1 \cdots \underset{\sim}{r}_\ell \rangle\right)^{n_\ell}$$

$$= \frac{1}{\Omega} \sum_{\{n_\ell\}} \prod_{\ell=1}^{N} \frac{\Omega^{n_\ell}}{\ell^{n_\ell}\, n_\ell!} (\ell!\; b_\ell(\text{cycle}))^{n_\ell}$$

$$= \frac{1}{\Omega} \sum_{\{n_\ell\}} \prod_{\ell=1}^{N} \frac{\Omega^{n_\ell}}{\ell^{n_\ell}\, n_\ell!} \left(\frac{1}{\lambda^3 \ell^{3/2}}\right)^{n_\ell} \tag{1.14}$$

To find the maximally contributing $\{n_\ell\}$, approximate the logarithm of $\lambda^3 b_N^S$ by its largest term.[4]

$$\ln \lambda^3 b_N^S \approx \ln \frac{\lambda^3}{\Omega} + \sum_{\ell=1}^{N} \left[n_\ell \ln \frac{\Omega}{\lambda^3} - \frac{5}{2} n_\ell \ln \ell - \ln n_\ell!\right] \tag{1.15}$$

Incorporate constraint (1.13) with $\ln z$ as a Lagrange multiplier and find extremum.

$$\delta\Big(\ln \lambda^3 b_N^S + \sum_{\ell=1}^{N} \ell n_\ell \ln z\Big) \approx$$

$$\sum_{\ell=1}^{N} \delta n_\ell \left[\ln \frac{\Omega}{\lambda^3} - \frac{5}{2} \ln \ell + \ell \ln z - \ln n_\ell\right] = 0 \tag{1.16}$$

$$n_\ell = \frac{\Omega\, z^\ell}{\lambda^3 \ell^{5/2}} \tag{1.17}$$

The density can be expressed as a series in z from (1.13)

$$\begin{aligned} \rho = \frac{N}{\Omega} &= \frac{\sum\limits_{\ell=1}^{N} \ell n_\ell}{\Omega} \\ &= \sum_{\ell=1}^{N} \frac{z^\ell}{\lambda^3 \ell^{3/2}} \end{aligned} \tag{1.18}$$

In the calculation of (1.9) and (1.11), the large volume limit was used, resulting in a loss of a term $\frac{1}{\ell} z^\ell$ in (1.17) and a term $\frac{1}{\Omega} z^\ell$ in (1.18). This "condensation" term can be understood as being due to a build up of particles in the zero-momentum state.

## C. Hard Sphere

We consider the hard-sphere pair-potentials

$$V[\underset{\sim}{X}_1(t) \ldots \underset{\sim}{X}_N(t)] = \sum_{i<j} V(\underset{\sim}{X}_i(t) - \underset{\sim}{X}_j(t)), \tag{1.19}$$

where

$$V(\underset{\sim}{X}_i(t) - \underset{\sim}{X}_j(t)) = \begin{cases} \infty, & |\underset{\sim}{X}_i(t) - \underset{\sim}{X}_j(t)| < a \\ 0, & |\underset{\sim}{X}_i(t) - \underset{\sim}{X}_j(t)| \geq a \end{cases} \tag{1.20}$$

This potential has the effect of excluding part of the total volume of the system, since any path $\underset{\sim}{X}_i(t)$ that brings one sphere close enough to any other sphere so that their volumes overlap is given the weight $e^{-\infty} = 0$. In calculating $b_N$(cycle) from (1.7) the integrals are all coupled together by the potential: the parts of $\int_\Omega d\underset{\sim}{r}_1$ that are excluded depend on the configuration of each of the other $\underset{\sim}{r}$'s. As an approximation, we neglect this dependence and reduce the available volume $\Omega$ by an amount $\Omega_{\text{excl}}$, which depends on the number and the size of the hard spheres.

$$\int_\Omega \cdots \int_\Omega \langle \underset{\sim}{r}_2 \cdots \underset{\sim}{r}_N \underset{\sim}{r}_1 | \exp(-\beta H_N) | \underset{\sim}{r}_1 \cdots \underset{\sim}{r}_N \rangle d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N =$$

$$\int_\Omega \cdots \int_\Omega d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N \Big( \int_{\underset{\sim}{r}_1}^{\underset{\sim}{r}_2} \cdots \int_{\underset{\sim}{r}_N}^{\underset{\sim}{r}_1} \mathcal{D}\underset{\sim}{X}_1(t) \cdots \mathcal{D}\underset{\sim}{X}_N(t) \exp[-\frac{1}{\hbar} \int_0^{\beta\hbar} dt \; \text{x}$$

$$\text{x} \; \{\tfrac{1}{2}M\dot{X}_1^2 + \ldots + \tfrac{1}{2}M\dot{X}_N^2 + V[\underset{\sim}{X}_1(t) \ldots \underset{\sim}{X}_N(t)]\}]\Big)$$

$$= \int_{\Omega-\Omega_{\text{excl}}} \cdots \int_{\Omega-\Omega_{\text{excl}}} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N \Big( \int_{\underset{\sim}{r}_1}^{\underset{\sim}{r}_2} \cdots \int_{\underset{\sim}{r}_N}^{\underset{\sim}{r}_1} \mathcal{D}\underset{\sim}{X}_1(t) \cdots \mathcal{D}\underset{\sim}{X}_N(t)$$

$$\text{x} \quad \exp[-\frac{1}{\hbar} \int_0^{\beta\hbar} dt \{\tfrac{1}{2}M\dot{X}_1^2 + \ldots + \tfrac{1}{2}M\dot{X}_N^2\}]\Big) \tag{1.21}$$

For high temperatures, when the thermal wavelength from (1.10)

$$\lambda = [\frac{2\pi\beta\hbar^2}{M}]^{\frac{1}{2}}$$

is much less than the hard sphere diameter a, (1.21) is approximately[5]

$$(1.21) = \frac{(\Omega-\Omega_{\mathrm{excl}})}{\lambda^3} \exp\{-\frac{N\pi^3(\frac{a}{\lambda})^2}{(N\ \sin\frac{\pi}{N})^2}\} \qquad (1.22)$$

which can be interpreted as the classical action for a uniform rotation of N particles equally spaced on a circle of radius $\frac{a}{(2\sin\frac{\pi}{N})}$ through the angle $\frac{2\pi}{N}$ in time $\beta\hbar$. For an estimate of the excluded volume, we use

$$\Omega_{\mathrm{excl}} = N\tfrac{4}{3}\pi a^3 = \rho\Omega\tfrac{4}{3}\pi a^3 \qquad (1.23)$$

and (1.21) becomes

$$(1.21) = (1-\rho\tfrac{4}{3}\pi a^3)\ \frac{\Omega}{\lambda^3} \exp\{-\frac{N\pi^3(\frac{a}{\lambda})^2}{(N\sin\frac{\pi}{N})^2}\} \qquad (1.24)$$

and the N-cyclic exchange cluster integral, (1.7), becomes

$$b_N(\mathrm{cycle}) = \frac{(1-\rho\frac{4}{3}\pi a^3)}{N!\ \lambda^3} \exp\{\frac{-N\pi^3(\frac{a}{\lambda})^2}{(N\sin\frac{\pi}{N})^2}\} \qquad (1.25)$$

The symmetrized N-particle cluster integral $b_N^S(\Omega)$ is calculated from (1.8) as it was for the ideal gas. In factoring the Green's function, we are neglecting part of the interactions between particles in different $\ell$-cycles; these are included only through the excluded volume.

$$b_N^S(\Omega) = \frac{1}{N!\Omega} \sum_{\{n_\ell\}} \frac{N!}{\prod_{\ell=1}^{N} \ell^{n_\ell} n_\ell!} \int_\Omega \cdots \int_\Omega d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N < \prod_{\ell=1}^{N} (\underset{\sim}{r}_2 \cdots \underset{\sim}{r}_\ell \underset{\sim}{r}_1)^{n_\ell} |$$

$$\times \exp(-\beta H_N) | \prod_{\ell'=1}^{N} (r_1 \cdots r_{\ell'})^{n_{\ell'}} > \qquad (1.26)$$

$$b_N^S(\Omega) = \frac{1}{\Omega} \sum_{\{n_\ell\}} \prod_{\ell=1}^{N} \frac{1}{\ell^{n_\ell} n_\ell!} \int_{\Omega-\Omega_{excl}} \cdots \int_{\Omega-\Omega_{excl}} d\underset{\sim}{r}_1 \cdots d\underset{\sim}{r}_N$$

$$\Big( \int_{\underset{\sim}{r}_1}^{\underset{\sim}{r}_2} \cdots \int_{\underset{\sim}{r}_\ell}^{\underset{\sim}{r}_1} \mathcal{D}\underset{\sim}{X}(t) \cdots \mathcal{D}\underset{\sim}{X}_\ell(t) \quad \times \tag{1.27}$$

$$\exp[-\frac{1}{\hbar} \int_0^{\beta\hbar} dt \{\tfrac{1}{2}M\dot{X}_1^2 + \ldots + \tfrac{1}{2}M\dot{X}_\ell^2\}]\Big)^{n_\ell}$$

$$\simeq \frac{1}{\Omega} \sum_{\{n_\ell\}} \prod_{\ell=1}^{N} \frac{\Omega^{n_\ell}}{\ell^{n_\ell} n_\ell!} (\ell!\ b_\ell(\text{cycle}))^{n_\ell}$$

$$b_N^S(\Omega) \simeq \frac{1}{\Omega} \sum_{\{n_\ell\}} \prod_{\ell=1}^{N} \frac{\Omega^{n_\ell}(1-\rho\frac{4}{3}\pi a^3)^{n_\ell}}{\ell^{n_\ell} n_\ell!\ \lambda^{3n_\ell}} \exp\{-\frac{n_\ell \ell\ \pi^3 (\frac{a}{\lambda})^2}{(\ell \sin\frac{\pi}{\ell})^2}\} \tag{1.28}$$

We find the set of maximally contributing $\{n_\ell\}$ subject to (1.13) as in (1.15) and (1.16):

$$\delta(\ell n \lambda^3 b_N^S + \sum_{\ell=1}^{N} \ell n_\ell \ell n z) \approx \tag{1.29}$$

$$\sum_{\ell=1}^{N} \delta n_\ell (\ell n[\frac{(1-\rho\frac{4}{3}\pi a^3)\Omega}{\lambda^3}] - \frac{\ell \pi^3 (\frac{a}{\lambda})^2}{(\ell \sin\frac{\pi}{\ell})^2} - \ell n \ell - \ell n\ n_\ell + \ell n z^\ell) = 0$$

$$n_\ell = \frac{(1-\rho\frac{4}{3}\pi a^3)\Omega}{\lambda^3 \ell} \exp\{-\frac{\ell \pi^3 (\frac{a}{\lambda})^2}{(\ell \sin\frac{\pi}{\ell})^2}\} z^\ell \tag{1.30}$$

As in (1.18) an expression for the density follows from (1.30).

$$\rho = \frac{N}{\Omega} = \frac{\sum_{\ell=1}^{N} \ell n_\ell}{\Omega}$$

$$= (1-\rho\tfrac{4}{3}\pi a^3) \sum_{\ell=1}^{N} \frac{\exp\{-\frac{\ell\pi^3(\frac{a}{\lambda})^2}{(\ell\sin\frac{\pi}{\ell})^2}\}\, z^\ell}{\lambda^3} \qquad (1.31)$$

Solving (1.31) for $\rho$

$$\rho = \frac{\sum_{\ell=1}^{N} \frac{1}{\lambda^3} \exp\{-\frac{\ell\pi^3(\frac{a}{\lambda})^2}{(\ell\sin\frac{\pi}{\ell})^2}\} z^\ell}{1 + \frac{4}{3}\pi a^3 \sum_{\ell=1}^{N} \frac{1}{\lambda^3} \exp\{-\frac{\ell\pi^3(\frac{a}{\lambda})^2}{(\ell\sin\frac{\pi}{\ell})^2}\} z^\ell} \qquad (1.32)$$

The condition (1.13) determining z is replaced by an implicit inversion of (1.32) the N-dependence of z is weak as is discussed later in Section D.

In the limit $N\to\infty$, the power series in z can possibly diverge. Even when it does, the density achieves at most the maximum value

$$\rho_{max} = \frac{1}{\frac{4}{3}\pi a^3} \qquad (1.33)$$

corresponding to an estimate of the close-packing of the particles.

The relative contribution of the $\ell$-cycle exchange is given by the fraction of the total number of particles that are in an $\ell$-cycle. Since $n_\ell$, given by (1.30) is the number of $\ell$-cycle exchanges, the likelihood of a particle being in an $\ell$-cycle is (for $\ell>1$)

$$P(\ell) = \frac{\ell n_\ell}{N} = \frac{1}{\lambda^3}\left(\frac{1}{\rho} - \frac{4}{3}\pi a^3\right)\exp\left\{-\frac{\ell\pi^3(\frac{a}{\lambda})^2}{(\ell\sin\frac{\pi}{\ell})^2}\right\} z^\ell \qquad (1.34)$$

The direct term is

$$P(1) = \frac{1}{\lambda^3}\left(\frac{1}{\rho} - \frac{4}{3}\pi a^3\right) z$$

The constraint (1.13) appears as a normalization condition in the $P(\ell)$.

$$\sum_{\ell=1}^{N} P(\ell) = \frac{\sum_{\ell=1}^{N} \ell n_\ell}{N} = 1 \qquad (1.35)$$

This is effected by the choice of z in (1.34).

## D. Numerical Simulation

A basis for a systematic comparison of the relative contributions of cycles of various lengths is provided by (1.34). In this section we present a numerical simulation to show how this approach is used to analyze trends in the behavior of the exchange terms as a function of temperature, density, and particle number.

It should be noted that (1.22) on which $P(\ell)$ in (1.34) is based was established for high temperatures and may have no direct application in a theory of the $\lambda$-transition.

The calculations presented here were performed on a Hewlett-Packard 9810 programmable calculator and used $a = 2\text{x}10^{-8}$ cm for the hard sphere diameter. The mass used in calculating the thermal wavelength was M = $6.67 \times 10^{-24}$ g. (These parameters are appropriate for $^4$He.)

The values of z were chosen so that the normalization condition (1.35) was properly satisfied. Comparing the columns of Tables 1-1 and 1-2, the effect of temperature on the exchange terms is simulated. In addition to the direct term, there is always a secondary peak in the $P(\ell)$. This secondary peak is never any lower than the three-cycle term. We see this in the last column of Table 1-2. As the temperature is decreased, this secondary peak shifts to the higher exchange terms and grows in comparison to the direct term. At very low temperatures this model predicts that the N-cycle exchange dominates even the direct term, as is seen in the first column of Table 1-1.

Comparing column two of Table 1-1 and the columns of Table 1-3, a similar effect is noted when the density is increased.

Table 1-4 compared to the second column of Table 1-1 shows how doubling the total number of particles changes the relative values of $P(\ell)$. There are more terms added to the series; the value of z must decrease to preserve the normalization; this damps the importance of the higher exchange terms. We note that the distributions are only weakly dependent on particle number.

Table 1-1

$N = 32 \qquad \rho = 2.14334 \times 10^{22}/cm^3$

| | $T = 1^0K$ | $T = 2^0K$ | $T = 5^0K$ |
|---|---|---|---|
| | $z = 1.2136563$ | $z = 1.3499414$ | $z = 1.9418053$ |
| $\ell$ | $P(\ell)$ | $P(\ell)$ | $P(\ell)$ |
| 1. | 0.024143 | 0.075955 | 0.431876 |
| 2. | 0.012939 | 0.019995 | 0.014082 |
| 3. | 0.017197 | 0.032368 | 0.043061 |
| 4. | 0.019059 | 0.036437 | 0.053098 |
| 5. | 0.020333 | 0.038006 | 0.054107 |
| 6. | 0.021378 | 0.038505 | 0.051269 |
| 7. | 0.022316 | 0.038454 | 0.046863 |
| 8. | 0.023199 | 0.038088 | 0.041962 |
| 9. | 0.024055 | 0.037529 | 0.037088 |
| 10. | 0.024899 | 0.036850 | 0.032495 |
| 11. | 0.025740 | 0.036093 | 0.028294 |
| 12. | 0.026585 | 0.035287 | 0.024525 |
| 13. | 0.027440 | 0.034452 | 0.021185 |
| 14. | 0.028307 | 0.033601 | 0.018250 |
| 15. | 0.029188 | 0.032743 | 0.015689 |
| 16. | 0.030087 | 0.031885 | 0.013465 |
| 17. | 0.031005 | 0.031032 | 0.011539 |
| 18. | 0.031943 | 0.030188 | 0.009878 |
| 19. | 0.032904 | 0.029355 | 0.008447 |
| 20. | 0.033888 | 0.028536 | 0.007218 |
| 21. | 0.034896 | 0.027732 | 0.006163 |
| 22. | 0.035930 | 0.026945 | 0.005259 |
| 23. | 0.036990 | 0.026174 | 0.004486 |
| 24. | 0.038079 | 0.025420 | 0.003824 |
| 25. | 0.039196 | 0.024684 | 0.003259 |
| 26. | 0.040344 | 0.023967 | 0.002776 |
| 27. | 0.041522 | 0.023267 | 0.002364 |
| 28. | 0.042732 | 0.022584 | 0.002013 |
| 29. | 0.043975 | 0.021920 | 0.001713 |
| 30. | 0.045253 | 0.021273 | 0.001458 |
| 31. | 0.046565 | 0.020644 | 0.001240 |
| 32. | 0.047914 | 0.020032 | 0.001055 |

Table 1-2

N = 32 $\rho = 2.14334 \times 10^{22}/\text{cm}^3$

|  | $T = 8^0K$<br>$z = 2.101957118$ | $T = 15^0K$<br>$z = .865277773$ | $T = 50^0K$<br>$z = .1421826939$ |
|---|---|---|---|
| ℓ | P(ℓ) | P(ℓ) | P(ℓ) |
| 1. | 0.946144 | 0.999979 | 1.000000000 00 |
| 2. | 0.002876 | 0.000004 | 2.534195613-19 |
| 3. | 0.012500 | 0.000014 | 3.379081901-18 |
| 4. | 0.012705 | 0.000003 | 5.123109185-21 |
| 5. | 0.009518 | 0.000000 | 1.153729571-24 |
| 6. | 0.006348 | 0.000000 | 1.255716364-28 |
| 7. | 0.003997 | 0.000000 | 9.538019178-33 |
| 8. | 0.002435 | 0.000000 | 5.894916247-37 |
| 9. | 0.001452 | 0.000000 | 3.199310477-41 |
| 10. | 0.000855 | 0.000000 | 1.590811069-45 |
| 11. | 0.000498 | 0.000000 | 7.435052672-50 |
| 12. | 0.000288 | 0.000000 | 3.320354857-54 |
| 13. | 0.000166 | 0.000000 | 1.432568936-58 |
| 14. | 0.000095 | 0.000000 | 6.017641939-63 |
| 15. | 0.000054 | 0.000000 | 2.474741659-67 |
| 16. | 0.000031 | 0.000000 | 1.000484280-71 |
| 17. | 0.000017 | 0.000000 | 3.988560857-76 |
| 18. | 0.000010 | 0.000000 | 1.571761635-80 |
| 19. | 0.000006 | 0.000000 | 6.133882269-85 |
| 20. | 0.000003 | 0.000000 | 2.374155187-89 |
| 21. | 0.000002 | 0.000000 | 9.124901339-94 |
| 22. | 0.000001 | 0.000000 | 0.000000000 00 |
| 23. | 0.000001 | 0.000000 | 0.000000000 00 |
| 24. | 0.000000 | 0.000000 | 0.000000000 00 |
| 25. | 0.000000 | 0.000000 | 0.000000000 00 |
| 26. | 0.000000 | 0.000000 | 0.000000000 00 |
| 27. | 0.000000 | 0.000000 | 0.000000000 00 |
| 28. | 0.000000 | 0.000000 | 0.000000000 00 |
| 29. | 0.000000 | 0.000000 | 0.000000000 00 |
| 30. | 0.000000 | 0.000000 | 0.000000000 00 |
| 31. | 0.000000 | 0.000000 | 0.000000000 00 |
| 32. | 0.000000 | 0.000000 | 0.000000000 00 |

# Table 1-3

| | $N = 32$ $T = 2^0$K | | |
|---|---|---|---|
| | $\rho = 2.357674 \times 10^{22}/\text{cm}^3$ | $\rho = 2.5934414 \times 10^{22}/\text{cm}^3$ | $= 2.85278554 \times 10^{22}/\text{cm}^3$ |
| | $z = 1.384328113$ | $z = 1.42901014$ | $z = 1.51111405$ |
| $\ell$ | $P(\ell)$ | $P(\ell)$ | $P(\ell)$ |
| 1. | 0.052759 | 0.030878 | 0.009981 |
| 2. | 0.014242 | 0.008605 | 0.002941 |
| 3. | 0.023643 | 0.014745 | 0.005329 |
| 4. | 0.027293 | 0.017571 | 0.006716 |
| 5. | 0.029193 | 0.019401 | 0.007841 |
| 6. | 0.030330 | 0.020807 | 0.008893 |
| 7. | 0.031062 | 0.021997 | 0.009941 |
| 8. | 0.031549 | 0.023063 | 0.011022 |
| 9. | 0.031879 | 0.024056 | 0.012157 |
| 10. | 0.032099 | 0.025004 | 0.013362 |
| 11. | 0.032240 | 0.025925 | 0.014650 |
| 12. | 0.032324 | 0.026831 | 0.016033 |
| 13. | 0.032363 | 0.027730 | 0.017523 |
| 14. | 0.032367 | 0.028629 | 0.019130 |
| 15. | 0.032344 | 0.029532 | 0.020867 |
| 16. | 0.032299 | 0.030443 | 0.022747 |
| 17. | 0.032235 | 0.031364 | 0.024781 |
| 18. | 0.032157 | 0.032298 | 0.026985 |
| 19. | 0.032067 | 0.033247 | 0.029374 |
| 20. | 0.031967 | 0.034212 | 0.031964 |
| 21. | 0.031857 | 0.035196 | 0.034772 |
| 22. | 0.031741 | 0.036199 | 0.037818 |
| 23. | 0.031618 | 0.037223 | 0.041122 |
| 24. | 0.031490 | 0.038269 | 0.044707 |
| 25. | 0.031357 | 0.039337 | 0.048596 |
| 26. | 0.031221 | 0.040430 | 0.052816 |
| 27. | 0.031081 | 0.041548 | 0.057395 |
| 28. | 0.030939 | 0.042693 | 0.062364 |
| 29. | 0.030793 | 0.043864 | 0.067756 |
| 30. | 0.030646 | 0.045063 | 0.073608 |
| 31. | 0.030497 | 0.046292 | 0.079959 |
| 32. | 0.030347 | 0.047550 | 0.086851 |

Table 1-4

$N = 64$ $\rho = 2.14334 \times 10^{22}/\text{cm}^3$

$T = 2^0\text{K}$ $z = 1.328709409$

| $\ell$ | $P(\ell)$ | $\ell$ | $P(\ell)$ |
|---|---|---|---|
| 1. | 0.074761 | 33. | 0.011519 |
| 2. | 0.019371 | 34. | 0.011000 |
| 3. | 0.030864 | 35. | 0.010504 |
| 4. | 0.034198 | 36. | 0.010030 |
| 5. | 0.035109 | 37. | 0.009577 |
| 6. | 0.035011 | 38. | 0.009144 |
| 7. | 0.034415 | 39. | 0.008730 |
| 8. | 0.033551 | 40. | 0.008334 |
| 9. | 0.032539 | 41. | 0.007957 |
| 10. | 0.031447 | 42. | 0.007596 |
| 11. | 0.030317 | 43. | 0.007251 |
| 12. | 0.029174 | 44. | 0.006922 |
| 13. | 0.028036 | 45. | 0.006607 |
| 14. | 0.026913 | 46. | 0.006307 |
| 15. | 0.025813 | 47. | 0.006020 |
| 16. | 0.024741 | 48. | 0.005746 |
| 17. | 0.023701 | 49. | 0.005484 |
| 18. | 0.022694 | 50. | 0.005234 |
| 19. | 0.021721 | 51. | 0.004996 |
| 20. | 0.020783 | 52. | 0.004768 |
| 21. | 0.019879 | 53. | 0.004551 |
| 22. | 0.019011 | 54. | 0.004343 |
| 23. | 0.018177 | 55. | 0.004145 |
| 24. | 0.017376 | 56. | 0.003956 |
| 25. | 0.016607 | 57. | 0.003775 |
| 26. | 0.015871 | 58. | 0.003603 |
| 27. | 0.015165 | 59. | 0.003439 |
| 28. | 0.014489 | 60. | 0.003281 |
| 29. | 0.013841 | 61. | 0.003132 |
| 30. | 0.013222 | 62. | 0.002988 |
| 31. | 0.012629 | 63. | 0.002852 |
| 32. | 0.012062 | 64. | 0.002722 |

# FOOTNOTES

1. T. D. Lee and C. N. Yang, Phys. Rev. 113, 1165 (1959).
2. The 1/N! in (1.7) is used for consistency with Lee & Yang cited above. Other authors,(e.g., below) do not have this factor. The results of this chapter do not depend on which of these definitions we use.
3. T. L. Hill, Statistical Mechanics, Chapter 5 (McGraw-Hill, N.Y., 1956).
4. J. E. Mayer and M. G. Mayer, Statistical Mechanics, Chapter 13 (Wiley, N.Y., 1940).
5. L. W. Bruch, Prog. Theor. Phys. 50, 1835 (1973).

# CHAPTER 2

# A NOTE ON COMPOSITE PARTICLE STATISTICS

> "Why is it that particles with half-integral spin are Fermi particles..., whereas particles with integral spin are Bose particles...?... The explanation is deep down in relativistic quantum mechanics. This probably means that we do not have a complete understanding of the fundamental principle involved."
>
> R. P. Feynman
> Lectures in Physics, Vol. III

The statistics of a particle composed of several elementary particles has been of interest for many years. Ehrenfest and Oppenheimer[1] concluded that nuclei obeyed Bose-Einstein or Fermi-Dirac statistics according to whether the number of particles in the nuclei was even or odd. More recently M. Girardeau[2] has studied the problem in the context of Bose-Condensation in $^4$He.

As the only stable massive particles are fermions, the extent to which composite particles of fermions behave as bosons is of interest in exchange phenomena.

We comment on several questions that arise. (i) What is the formal procedure for treating composite particles? (ii) What restrictions are there on the regarding of composite particles as bosons? (iii) Where does the formalism prevent us from treating the wrong things as bosons?

## A. Second Quantized States

To discuss the statistics of many-particle systems, we use the second-quantized formalism. In this approach, all physical observables are assumed to be elements of the algebra generated by a set of creation and annihilation operators. The particle statistics is incorporated in the algebra, whose generators obey a set of canonical commutation relations in the case of bosons or a set of canonical anticommutation relations in the case of fermions.

Denote the boson creation and annihilation operators by $a_\alpha^+$ and $a_\alpha$, respectively. The index $\alpha$ carries the momentum and spin information about the states. The canonical commutation relations (CCR) are the set

$$\begin{aligned} [a_\alpha^+, a_{\alpha'}^+] &= 0 \\ [a_\alpha, a_{\alpha'}] &= 0 \\ [a_\alpha, a_{\alpha'}^+] &= \delta_{\alpha\alpha'} \end{aligned} \tag{2.1}$$

in which the bracket denotes the commutator.

Denote the corresponding fermion operators by $C_\alpha^+$ and $C_\alpha$. The canonical anticommutation relations (CAR) are the set

$$\begin{aligned} \{C_\alpha^+, C_{\alpha'}^+\} &= 0 \\ \{C_\alpha, C_{\alpha'}\} &= 0 \\ \{C_\alpha, C_{\alpha'}^+\} &= \delta_{\alpha\alpha'} \end{aligned} \tag{2.2}$$

in which the curly bracket denotes the anticommutator.

States are representable by particle creation operators acting on a state $|0>$, the vacuum state. There are many representations possible depending on which state $|0>$ is used to define the vacuum. The n-particle state is

$$a^{+}_{\alpha_1} \ldots a^{+}_{\alpha_n} |0>. \tag{2.3}$$

If $\phi_\alpha(x)$ is a one-particle wave function, the relation to the second quantized representation is given by

$$a^{+}_{\alpha} = \int dx\ \phi_\alpha(x)\ \phi^{+}(x) \tag{2.4}$$

for bosons, or

$$c^{+}_{\alpha} = \int dx\ \phi_\alpha(x)\ \psi^{+}(x) \tag{2.5}$$

for fermions. $\phi^{+}(x)$ and $\psi^{+}(x)$ in (2.4) and (2.5) are the position representations of the CCR and the CAR algebras. These satisfy:

$$\begin{aligned} [\phi^{+}(x),\ \phi^{+}(x')] &= 0 \\ [\phi(x),\ \phi(x')] &= 0 \\ [\phi(x),\ \phi^{+}(x')] &= \delta(x-x') \end{aligned} \tag{2.6}$$

$$\begin{aligned} \{\psi^{+}(x),\ \psi^{+}(x')\} &= 0 \\ \{\psi(x),\ \psi(x')\} &= 0 \\ \{\psi(x),\ \psi^{+}(x')\} &= \delta(x-x') \end{aligned} \tag{2.7}$$

## B. Bose Condensation of the Ideal Gas

For a system of bosons, considering only the momentum k in the index α, the one particle state (2.3) is

$$|k\rangle = a_k^+|0\rangle \tag{2.8}$$

and the ℓ-particle state

$$|k_1 \ldots k_\ell\rangle = a_{k_1}^+ \ldots a_{k_\ell}^+ |0\rangle \qquad (2.9$$

The free-particle Hamiltonian is

$$H_\ell = \sum_{i=1}^{\ell} \frac{\hbar^2 k_i^2}{2M} = \sum_k a_k^+ a_k \frac{\hbar^2 k^2}{2M} \tag{2.10}$$

$$\begin{aligned} \langle k'|\exp(-\frac{\beta\hbar^2 k^2}{2M})|k\rangle &= \langle 0|a_{k'} \exp(-\frac{\beta\hbar^2 k^2}{2M}) a_k^+|0\rangle \\ &= \delta_{kk'} \exp(-\frac{\beta\hbar^2 k^2}{2M}) \end{aligned} \tag{2.11}$$

The symmetrized cluster integral discussed in (1.14) has the form

$$b_\ell^S = \sum_{\substack{k_1 \ldots k_\ell \\ k_1' \ldots k_\ell'}} \frac{1}{\ell\Omega} \prod_{j=1}^{\ell} \langle k_j'|\exp(-\frac{\beta\hbar^2 k^2}{2M})|k_j\rangle \tag{2.12}$$

(2.11) and (2.12) give

$$b_\ell^S = \frac{1}{\ell\Omega} \sum_k \exp(-\ell\beta\frac{\hbar^2 k^2}{2M}) \tag{2.13}$$

and the density series

$$\rho = \sum_{\ell} \ell \, b_{\ell}^{S} z^{\ell}$$

$$= \frac{1}{\Omega} \sum_{k} \frac{\exp(-\frac{\beta\hbar^2 k^2}{2M})\, z}{1-\exp(-\frac{\beta\hbar^2 k^2}{2M})\, z} = \frac{N}{\Omega} \qquad (2.14)$$

which can give a build-up of particles in the k=0 state.

## C. Composite Particle Commutation Relations

In the conventional explanation of superfluidity in $^4$He, the atom is treated as a boson and the arguments of the previous section are taken as a model.[3] Treating the $^4$He nucleus as a boson, we can think of the atom as made up of three particles, one nucleus and two electrons. The atomic electrons have an exchange interaction with other atomic electrons because of their fermi-statistics. This exchange interaction depends on how much the electron wavefunctions overlap. Conventionally, this interaction enters into the energy in the atomic pair-potentials. These exchange effects of the electrons affect the extent to which the atom can be treated as a boson.

Let $\Phi_\alpha(x_1 \ldots x_{mb}, y_1 \ldots y_{mf})$ be the wavefunction for a composite particle of $m_b$ bosons and $m_f$ fermions. Operators for this composite particle can be constructed[4]

$$A_\alpha^+ = \frac{1}{\sqrt{(m_b)!(m_f)!}} \int dx_1 \ldots dx_{mb} dy_1 \ldots dy_{mf} \, \Phi_\alpha(x_1 \ldots x_{mb} y_1 \ldots y_{mf})$$

$$\times \, \phi^+(x_1) \ldots \phi^+(x_{mb}) \psi^+(y_1) \ldots \psi^+(y_{mf})$$

$$A_\alpha = \frac{1}{\sqrt{(m_b)!(m_f)!}} \int dx_1 \ldots dx_{mb} dy_1 \ldots dy_{mf} \, \Phi_\alpha(x_1 \ldots x_{mb} y_1 \ldots y_{mf}) \times \phi(x_{mb}) \ldots \phi(x_1) \psi(y_{mf}) \ldots \psi(y_1) \tag{2.15}$$

The commutation relations of $A^+_\alpha$ and $A_\alpha$ are induced from those of the particles of which they are composed. From (2.15)

$$\begin{aligned}[A_\alpha, A^+_{\alpha'}] = \frac{1}{(m_b)!(m_f)!} & \int dx_1 \ldots dx_{mb} dy_1 \ldots dy_{mf} dx'_1 \ldots dx'_{mb} dy'_1 \ldots dy'_{mf} \\ & \times \Phi^*_\alpha(x_1 \ldots x_{mb} y_1 \ldots y_{mf}) \Phi_{\alpha'}(x'_1 \ldots x'_{mb} y'_1 \ldots y'_{mf}) \\ & \times [\psi(y_{mf}) \ldots \psi(y_1) \phi(x_{mb}) \ldots \phi(x_1), \\ & \qquad \phi^+(x'_1) \ldots \phi^+(x'_{mb}) \psi^+(y'_1) \ldots \psi^+(y_{mf})]\end{aligned} \tag{2.16}$$

If the composite particle is made up of one boson only, then from (2.1) or (2.6),

$$[A_\alpha, A^+_{\alpha'}] = \delta_{\alpha\alpha'}$$

If it is made up of one fermion, then from (2.2)

$$\begin{aligned}[A_\alpha, A^+_{\alpha'}] &= [C_\alpha, C^+_{\alpha'}] = C_\alpha C^+_{\alpha'} - C^+_{\alpha'} C_\alpha \\ &= \delta_{\alpha\alpha'} - 2C^+_{\alpha'} C_\alpha \\ &= \delta_{\alpha\alpha'} - 2\int dx' dx \, \Phi_{\alpha'}(x') \Phi^*_\alpha(x) \psi^+(x') \psi(x)\end{aligned} \tag{2.17}$$

By considering examples, it is not difficult to see that in general

$$[A_\alpha, A^+_{\alpha'}] = \delta_{\alpha\alpha'} + C_{\alpha\alpha'} \qquad (2.18)$$

where $C_{\alpha\alpha'}$ is a combination of normal ordered terms with integrals of the wavefunctions. In certain physical cases, it can be argued that such overlap integrals are small in comparison to one. Thus the condition for an approximate Bose statistic

$$[A_\alpha, A^+_{\alpha'}] \approx \delta_{\alpha\alpha'} \qquad (2.19)$$

appears to be not too restrictive.

In considering the other two relations in (2.1), we see that constraints enter on the type of composite particle we can treat as being a boson. From (2.15)

$$\begin{aligned}[A^+_\alpha, A^+_{\alpha'}] = {} & \frac{1}{(m_b)!(m_f)!} \int dx_1 \ldots dx_{mb}\, dy_1 \ldots dy_{mf}\, dx'_1 \ldots dx'_{mb}\, dy'_1 \ldots dy'_{mf} \\ & \times \Phi_\alpha(x_1 \ldots x_{mb} y_1 \ldots y_{mf}) \Phi_{\alpha'}(x'_1 \ldots x'_{mb} y'_1 \ldots y'_{mf}) \\ & \times [\phi^+(x_1) \ldots \phi^+(x_{mb}) \psi^+(y_1) \ldots \psi^+(y_{mf}), \qquad (2.20) \\ & \quad \phi^+(x'_1) \ldots \phi^+(x'_{mb}) \psi^+(y'_1) \ldots \psi^+(y'_{mf})]\end{aligned}$$

Only in certain cases will (2.20)

$$[A^+_\alpha, A^+_{\alpha'}] = 0$$

as in (2.1). As an example, consider the case of a composite particle of two fermions. In computing $[A^+_\alpha, A^+_{\alpha'}]$ from (2.20), using (2.7), the factor

$$[\psi^+(y_1)\psi^+(y_2),\psi^+(y_1')\psi^+(y_2')]$$

$$= \psi^+(y_1)\psi^+(y_2)\psi^+(y_1')\psi^+(y_2')-\psi^+(y_1')\psi^+(y_2')\psi^+(y_1)\psi^+(y_2)$$

$$= \psi^+(y_1')\psi^+(y_2')\psi^+(y_1)\psi^+(y_2)-\psi^+(y_1')\psi^+(y_2')\psi^+(y_1)\psi^+(y_2)$$

$$= 0 \tag{2.21}$$

(2.21) in (2.20) gives

$$[A_\alpha^+,A_{\alpha'}^+] = 0$$

for a bound pair of electrons.

Girardeau has exhibited a formal connection between the composite particle operators $A_\alpha, A_\alpha^+$ and the operators $a_\alpha$, $a_\alpha^+$ of an ideal boson. His procedure amounts to an algebra automorphism between these two. He executes this through a unitary transformation U such that

$$\begin{gathered} U\, A_\alpha^+|0\rangle = a_\alpha^+|0\rangle \\ U\, A_{\alpha_1}^+ \ldots A_{\alpha_n}^+ |0\rangle \approx a_{\alpha_1}^+ \ldots a_{\alpha_n}^+ |0\rangle \end{gathered} \tag{2.22}$$

i.e., the state of one composite particle is transformed to the one boson state, and the many composite-particle state is approximately mapped to the many boson state to the extent that overlap integrals are small.

## D. Counterexamples

If we try to apply this prescription to composite particles that are very non-boson in nature, we will get contradictions. To see this, consider the case, where we try to transform a system of fermions obeying (2.2) into a set of bosons.

$$A^+_\alpha = C^+_\alpha \qquad A_\alpha = C_\alpha \tag{2.23}$$

(2.23) into (2.25) means we assume that there exists some U such that

$$U\ C^+_\alpha|0> = a^+_\alpha|0> \qquad U\ C^+_{\alpha_1}\ldots C^+_{\alpha_n}|0> = a^+_{\alpha_1}\ldots a^+_{\alpha_n}|0> \tag{2.24}$$

(2.2) implies the Pauli exclusion principle

$$C^+_\alpha C^+_\alpha = -C^+_\alpha C^+_\alpha = 0 \tag{2.25}$$

(2.25) implies that

$$C^+_\alpha C^+_\alpha C^+_\alpha = -C^+_\alpha C^+_\alpha C^+_\alpha = 0$$

and

$$U\ C^+_\alpha C^+_\alpha C^+_\alpha|0> = U\ C^+_\alpha C^+_\alpha|0> \tag{2.26}$$

But

$$U\ C^+_\alpha C^+_\alpha|0> \approx a^+_\alpha a^+_\alpha|0> \qquad U\ C^+_\alpha C^+_\alpha C^+_\alpha|0> \approx a^+_\alpha a^+_\alpha a^+_\alpha|0> \tag{2.27}$$

(2.27) is a contradiction because

$$a^+_\alpha a^+_\alpha a^+_\alpha |0> \neq a^+_\alpha a^+_\alpha |0>$$

thus no such U can be defined.

Even restricting ourselves to a sub-algebra of the $a^+_\alpha$, $a_\alpha$ obeying the Exclusion Principle, i.e., restricting our set of states to those where no more than one particle is in any given state does not help. By (2.2)

$$C^+_{\alpha_1} C^+_{\alpha_2} = -C^+_{\alpha_2} C^+_{\alpha_1}$$

and
$$C^+_{\alpha_1} C^+_{\alpha_2} |0> = -C^+_{\alpha_2} C^+_{\alpha_1} |0> \qquad (2.28)$$

$$U\ C^+_{\alpha_1} C^+_{\alpha_2} |0> = a^+_{\alpha_1} a^+_{\alpha_2} |0> = a^+_{\alpha_2} a^+_{\alpha_1} |0> \qquad (2.29)$$

By (2.28)

$$U\ C^+_{\alpha_1} C^+_{\alpha_2} |0> = U(-C^+_{\alpha_2} C^+_{\alpha_1})|0> = -U\ C^+_{\alpha_2} C^+_{\alpha_1} |0> \qquad (2.30)$$
$$= -a^+_{\alpha_2} a^+_{\alpha_1} |0>$$

(2.29) and (2.30) give the contradiction that

$$a^+_{\alpha_2} a^+_{\alpha_1} |0> = -a^+_{\alpha_2} a^+_{\alpha_1} |0>$$

so no such U can be defined for many particle systems.

# FOOTNOTES

1. P. Ehrenfest and J. R. Oppenheimer, Phys. Rev. 37, 333 (1931).
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3. F. London, *Superfluids*, (Wiley, N.Y., 1950).
4. M. D. Girardau, J. Math. Phys. 12, 1799 (1971).

# PART II

# THREE-BODY EXCHANGE EFFECTS: THE TRIMER

# CHAPTER 3

# EQUILATERAL TRIANGLE MODEL

In this chapter we present a simple model for discussing the problem of three particles bound together in three dimensions by pair-potentials. The three particles are assumed to be near the vertices of a rotating equilateral triangle.

The three-particle Schroedinger equation, which is in general insoluble in closed form, in this model readily separates into center of mass, vibrational, and rotational motion, each of which are solved for their contribution to the total energy. An ordering of the rotational states is noted for later consideration in connection with exchange restrictions.

## A. Center of Mass and Reduced Variables

Let $\psi(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3)$ be the trimer wavefunction; it depends on the nine coordinate components of the three particles. The Schrodinger equation for an energy eigenstate is

$$H\psi = -\frac{\hbar^2}{2M}\{\nabla^2_{\underset{\sim}{r}_1}+\nabla^2_{\underset{\sim}{r}_2}+\nabla^2_{\underset{\sim}{r}_3}\}\psi + V(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3)\psi = E\psi \tag{3.1}$$

$V(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3)$ is assumed to be due to pair potentials with an attractive part and a repulsive core. The minimum value of the pair potentials is taken to be at an interparticle separation of $r_o$. Near the equilibrium binding of the three particles, an harmonic oscillator approximation is made.

$$V(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) \simeq -3V_o + \frac{1}{2}V''(r_o)\{[|\underset{\sim}{r}_1-\underset{\sim}{r}_2|-r_o]^2 + [|\underset{\sim}{r}_2-\underset{\sim}{r}_3|-r_o]^2 + [|\underset{\sim}{r}_3-\underset{\sim}{r}_1|-r_o]^2\} \tag{3.2}$$

We use the three-body Jacobi coordinates, in which the center of mass

$$\underset{\sim}{R} = \frac{1}{3}(\underset{\sim}{r}_1+\underset{\sim}{r}_2+\underset{\sim}{r}_3) \tag{3.3}$$

and the reduced variables

$$\begin{aligned} \underset{\sim}{\rho} &= \underset{\sim}{r}_1-\underset{\sim}{r}_2 \\ \underset{\sim}{\sigma} &= \underset{\sim}{r}_3-\frac{1}{2}(\underset{\sim}{r}_1+\underset{\sim}{r}_2) \end{aligned} \tag{3.4}$$

are used to separate out the center of mass motion from the relative motion. (3.3) and (3.4) are inverted:

$$\begin{aligned} \underset{\sim}{r}_1 &= \underset{\sim}{R} + \frac{1}{2}\underset{\sim}{\rho} - \frac{1}{3}\underset{\sim}{\sigma} \\ \underset{\sim}{r}_2 &= \underset{\sim}{R} - \frac{1}{2}\underset{\sim}{\rho} - \frac{1}{3}\underset{\sim}{\sigma} \\ \underset{\sim}{r}_3 &= \underset{\sim}{R} + \frac{2}{3}\underset{\sim}{\sigma} \end{aligned} \tag{3.5}$$

From (3.3) and (3.4) it follows that

$$\begin{aligned}
\nabla_{\underset{\sim}{r}_1} &= \frac{1}{3}\nabla_{\underset{\sim}{R}} + \nabla_{\underset{\sim}{\rho}} - \frac{1}{2}\nabla_{\underset{\sim}{\sigma}} \\
\nabla_{\underset{\sim}{r}_2} &= \frac{1}{3}\nabla_{\underset{\sim}{R}} - \nabla_{\underset{\sim}{\rho}} - \frac{1}{2}\nabla_{\underset{\sim}{\sigma}} \qquad (3.6) \\
\nabla_{\underset{\sim}{r}_3} &= \frac{1}{3}\nabla_{\underset{\sim}{R}} + \nabla_{\underset{\sim}{\sigma}}
\end{aligned}$$

and

$$(\nabla^2_{\underset{\sim}{r}_1} + \nabla^2_{\underset{\sim}{r}_2} + \nabla^2_{\underset{\sim}{r}_3})\psi = (\frac{1}{3}\nabla^2_{\underset{\sim}{R}} + 2\nabla^2_{\underset{\sim}{\rho}} + \frac{3}{2}\nabla^2_{\underset{\sim}{\sigma}})\psi \qquad (3.7)$$

(3.6) into (3.1) and (3.5) into (3.2) give

$$\begin{aligned}
&-\frac{\hbar^2}{2(3M)}\nabla^2_{\underset{\sim}{R}}\psi - \frac{\hbar^2}{2(M/2)}\nabla^2_{\underset{\sim}{\rho}}\psi - \frac{\hbar^2}{2(2M/3)}\nabla^2_{\underset{\sim}{\sigma}}\psi - 3V_o\psi \\
&\quad + \frac{1}{2}V''(r_o)\{[|\underset{\sim}{\rho}|-r_o]^2 + [|-\frac{1}{2}\underset{\sim}{\rho}-\underset{\sim}{\sigma}|-r_o]^2 + [|\underset{\sim}{\sigma}-\frac{1}{2}\underset{\sim}{\rho}|-r_o]^2\}\psi \\
&\quad = E\psi \qquad (3.8)
\end{aligned}$$

The first term corresponds to the center of mass motion and its contribution to the total energy. Since the potential does not depend on $\underset{\sim}{R}$, the center-of-mass part of $\psi$ is just that of a free particle of mass (3M) and an energy $E_{c.m.}$.

## B. Vibrational Energy

The relative coordinates $\underset{\sim}{\rho}$ and $\underset{\sim}{\sigma}$ are measured in the space-fixed frame. In view of the nearly-rigid character of this trimer model and for notational convenience, look at the motion when $\underset{\sim}{\rho}$ is nearly along the space-fixed x-axis and $\underset{\sim}{\sigma}$ is nearly along the space-fixed y-axis. We do this as an initial choice of axes and do not assume this as a continuing restriction.

$$\begin{aligned}\underset{\sim}{\rho}&=r_o\hat{x} + \Delta\rho_x\hat{x} + \Delta\rho_y\hat{y} + \Delta\rho_z\hat{z}\\ \underset{\sim}{\sigma} &= \frac{\sqrt{3}}{2}r_o\hat{y} + \Delta\sigma_x\hat{x} + \Delta\sigma_y\hat{y} + \Delta\sigma_z\hat{z}\end{aligned} \tag{3.9}$$

In order to separate the vibrational motion, we introduce the normal coordinates which are found classically (Goldstein).

$$\begin{aligned}\eta_1 &= \frac{1}{\sqrt{3}}\Delta\sigma_y + \frac{1}{2}\Delta\rho_x\\ \eta_2 &= \frac{1}{\sqrt{3}}\Delta\sigma_y - \frac{1}{2}\Delta\rho_x\\ \eta_3 &= \frac{1}{\sqrt{3}}\Delta\sigma_x + \frac{1}{2}\Delta\rho_y\\ \eta_4 &= \frac{1}{\sqrt{3}}\Delta\sigma_x - \frac{1}{2}\Delta\rho_y\end{aligned} \tag{3.10}$$

Inverting these,

$$\begin{aligned}
\Delta\rho_x &= (\eta_1-\eta_2)\\
\Delta\rho_y &= (\eta_3-\eta_4)\\
\Delta\sigma_x &= \frac{\sqrt{3}}{2}(\eta_3+\eta_4)\\
\Delta\sigma_y &= \frac{\sqrt{3}}{2}(\eta_1+\eta_2)
\end{aligned} \qquad (3.11)$$

(3.11) into (3.9) gives

$$\begin{aligned}
\underset{\sim}{\rho} &= r_o\hat{x} + (\eta_1-\eta_2)\hat{x} + (\eta_3-\eta_4)\hat{y} + \Delta\rho_z\hat{z}\\
\underset{\sim}{\sigma} &= \frac{\sqrt{3}}{2}r_o\hat{y} + \frac{\sqrt{3}}{2}(\eta_3+\eta_4)\hat{x} + \frac{\sqrt{3}}{2}(\eta_1+\eta_2)\hat{y} + \Delta\sigma_z\hat{z}
\end{aligned} \qquad (3.12)$$

(3.12) gives

$$\begin{aligned}
\frac{\partial}{\partial\Delta\rho_x} &= \frac{1}{2}\left[\frac{\partial}{\partial\eta_1} - \frac{\partial}{\partial\eta_2}\right]\\
\frac{\partial}{\partial\Delta\rho_y} &= \frac{1}{2}\left[\frac{\partial}{\partial\eta_3} - \frac{\partial}{\partial\eta_4}\right]\\
\frac{\partial}{\partial\Delta\sigma_x} &= \frac{1}{\sqrt{3}}\left[\frac{\partial}{\partial\eta_3} + \frac{\partial}{\partial\eta_4}\right]\\
\frac{\partial}{\partial\Delta\sigma_y} &= \frac{1}{\sqrt{3}}\left[\frac{\partial}{\partial\eta_1} + \frac{\partial}{\partial\eta_2}\right]
\end{aligned} \qquad (3.13)$$

(3.12) and (3.13) into (3.8) give

$$\begin{aligned}
&-\frac{h^2}{2(\frac{M}{2})}\left\{\frac{\partial^2}{\partial\Delta\rho_x^2} + \frac{\partial^2}{\partial\Delta\rho_y^2} + \frac{\partial^2}{\partial\Delta\rho_z^2}\right\}\psi - \frac{h^2}{2(\frac{2M}{3})}\left\{\frac{\partial^2}{\partial\Delta\sigma_x^2} + \frac{\partial^2}{\partial\Delta\sigma_y^2} + \frac{\partial^2}{\partial\Delta\sigma_z^2}\right\}\psi\\
&+ \frac{1}{2}V''(r_o)\left\{[|\underset{\sim}{\rho}|-r_o]^2 + [|-\tfrac{1}{2}\underset{\sim}{\rho}-\underset{\sim}{\sigma}|-r_o]^2 + [|\underset{\sim}{\sigma}-\tfrac{1}{2}\underset{\sim}{\rho}|-r_o]^2\right\}\psi\\
&= (E-E_{cm}+3V_o)\psi
\end{aligned}$$

$$= -\frac{\hbar}{2M}\{\frac{\partial^2}{\partial\eta_1^2} + \frac{\partial^2}{\partial\eta_2^2} + \frac{\partial^2}{\partial\eta_3^2} + \frac{\partial^2}{\partial\eta_4^2} + 2\frac{\partial^2}{\partial\Delta\rho_z^2} + \frac{3}{2}\,\frac{\partial^2}{\partial\Delta\sigma_z^2}\}\psi$$

$$+ \frac{1}{2}\,V''(r_o)\{3\,\eta_1^2 + \frac{3}{2}\,\eta_2^2 + \frac{3}{2}\,\eta_3^2\}\psi \qquad (3.14)$$

Note that $\eta_4$ is an "ignorable" coordinate as a vibration. Later we will see that it corresponds to a rotation. The other rotational motions come from the displacement coordinate of $\underset{\sim}{\rho}$ and $\underset{\sim}{\sigma}$ perpendicular to the plane. In (3.12) these are $\Delta\rho_z$ and $\Delta\sigma_z$. The vibrational motion of the particles about the equilibrium separation $r_o$ separates; $\psi$ can be written as a product of three harmonic oscillator wavefunctions in $\eta_1$, $\eta_2$, $\eta_3$, and the remaining function of $\eta_4$, $\Delta\rho_z$, $\Delta\sigma_z$. The harmonic oscillator frequencies are

$$\omega_1 = \sqrt{\frac{3V''(r_o)}{M}}$$

$$\omega_2 = \omega_3 = \sqrt{\frac{3V''(r_o)}{2M}} \qquad (3.15)$$

Each oscillator part has ground state energy $\frac{1}{2}\hbar\omega_i$, so that the total vibrational energy

$$E_v = \frac{1}{2}\hbar\omega_1 + \frac{1}{2}\hbar\omega_2 + \frac{1}{2}\hbar\omega_3$$

$$= \frac{1}{2}\hbar(\sqrt{3} + 2\sqrt{\frac{3}{2}})\quad\frac{V''(r_o)}{M} \qquad (3.16)$$

$$= (1 + \sqrt{2})\hbar\quad\frac{3V''(r_o)}{4M}$$

This vibrational energy is reviewed in Herzberg[1] and was calculated by Bruch and Stenschke[2] in a treatment of inert gas trimers. They also calculated the first anharmonic corrections to Eq. (3.16) arising from cubic and quartic terms dropped in Eq. (3.2).

## C. Rotational Energy

To discuss the rotational motion, we use a set of Euler angles $(\alpha,\beta,\gamma)$ with Edmond's convention.

$\alpha$ = counterclockwise rotation about the space-fixed z-axis

$\beta$ = counterclockwise rotation about the body-fixed y'-axis

$\gamma$ = counterclockwise rotation about the body-fixed z'-axis

The body-fixed z'-axis is taken perpendicular to the triangle of the particles. We ignore the effect of the zero-point motion treated in the previous section and treat the trimer as a rigid body, and let the body x'-axis move parallel to $\underset{\sim}{\rho}$, and the body-fixed y'-axis move with $\underset{\sim}{\sigma}$.

We wish to relate the remaining variables in our three body Schroedinger equation to the Euler angles and show that the rotational part of the Schroedinger equation takes the form of the quantum rigid rotor with moments of inertia $I_x = I_y = \frac{1}{2} M r_o^2$, $I_z = M r_o^2$. To do this we consider a classical triangle rotating with angular velocities $\omega_x$, $\omega_y$, and $\omega_z$. Using these classical angular velocities we motivate a set of formal differential relations of coordinates (3.22).

For a classical triangle, the changes in our remaining $\Delta\rho$, $\Delta\sigma$ coordinates can be related to rotational velocities by

$$\begin{aligned} \Delta\dot{\sigma}_z &= \omega_x \frac{\sqrt{3}}{2} r_o \\ \Delta\dot{\rho}_z &= -\omega_y r_o \\ \Delta\dot{\rho}_y &= \omega_z r_o \\ \Delta\dot{\sigma}_x &= -\omega_z \frac{\sqrt{3}}{2} r_o \end{aligned} \tag{3.17}$$

Note that

$$\begin{aligned} \dot{\eta}_4 &= \frac{1}{\sqrt{3}} \Delta\dot{\sigma} - \frac{1}{2} \Delta\dot{\rho}_y \\ &= -\frac{1}{2} \omega_z r_o - \frac{1}{2} \omega_z r_o \end{aligned} \tag{3.18}$$

$$\dot{\eta}_4 = -\omega_z r_o$$

From (3.17) and (3.18) the classical angular velocities are related to these coordinates by

$$\begin{aligned} \omega_x &= \frac{2\Delta\dot{\sigma}_z}{\sqrt{3}\, r_o} \\ \omega_y &= \frac{-\Delta\dot{\rho}_z}{r_o} \\ \omega_z &= \frac{-\dot{\eta}_4}{r_o} \end{aligned} \tag{3.19}$$

The classical geometric relations between angular velocity and the Euler angles are[3]

$$\begin{aligned} \omega_x &= \dot{\beta}\sin\gamma - \dot{\alpha}\sin\beta\,\cos\gamma \\ \omega_y &= \dot{\beta}\cos\gamma + \dot{\alpha}\sin\beta\,\sin\gamma \\ \omega_z &= \dot{\alpha}\cos\beta + \dot{\gamma} \end{aligned} \qquad (3.20)$$

Inverting (3.20)

$$\begin{aligned} \dot{\alpha} &= \frac{\omega_y\sin\gamma - \omega_x\cos\gamma}{\sin\beta} \\ \dot{\beta} &= \omega_y\cos\gamma + \omega_x\sin\gamma \\ \dot{\gamma} &= \omega_z - \frac{\cos\beta}{\sin\beta}(\omega_y\sin\gamma - \omega_x\cos\gamma) \end{aligned} \qquad (3.21)$$

Thus a set of differential relations between the Euler angle and our remaining coordinates $\Delta\rho_z$, $\Delta\sigma_z$, $\eta_4$ can be obtained by substituting (3.19) into (3.21).

$$\begin{aligned} d\alpha &= -\frac{1}{r_o}\frac{\sin\gamma}{\sin\beta}\,d\Delta\rho_z - \frac{2}{\sqrt{3}r_o}\frac{\cos\gamma}{\sin\beta}\,d\Delta\sigma_z \\ d\beta &= -\frac{1}{r_o}\cos\gamma\,d\Delta\rho_z + \frac{2}{\sqrt{3}r_o}\sin\gamma\,d\Delta\sigma_z \\ d\gamma &= -\frac{1}{r_o}\,d\eta_4 + \frac{\cos\beta}{\sin\beta}\left(\frac{1}{r_o}\sin\gamma\,d\Delta\rho_z + \frac{2}{\sqrt{3}r_o}\cos\gamma\,d\Delta\sigma_z\right) \end{aligned} \qquad (3.22)$$

(3.22) can now be taken over formally into the quantum trimer.

$$\frac{\partial}{\partial\eta_4} = -\frac{1}{r_o}\frac{\partial}{\partial\gamma}$$

$$\frac{\partial}{\partial\Delta\rho_z} = -\frac{1}{r_o}\frac{\sin\gamma}{\sin\beta}\frac{\partial}{\partial\alpha} - \frac{1}{r_o}\cos\gamma\frac{\partial}{\partial\beta} + \frac{1}{r_o}\frac{\cos\beta\sin\gamma}{\sin\beta}\frac{\partial}{\partial\gamma} \tag{3.23}$$

$$\frac{\partial}{\partial\Delta\sigma_z} = -\frac{2}{\sqrt{3}r_o}\frac{\cos\gamma}{\sin\beta}\frac{\partial}{\partial\alpha} + \frac{2}{\sqrt{3}r_o}\sin\gamma\frac{\partial}{\partial\beta} + \frac{2}{\sqrt{3}r_o}\frac{\cos\beta\cos\gamma}{\sin\beta}\frac{\partial}{\partial\gamma}$$

The reduced Schroedinger is now

$$-\frac{\hbar^2}{2M}\{\frac{\partial^2}{\partial\eta_4^2} + 2\frac{\partial^2}{\partial\Delta\rho_z^2} + \frac{3}{2}\frac{\partial^2}{\partial\Delta\sigma_z^2}\}\psi + (E_{cm}+E_v-3V_o)\psi=E\psi \tag{3.24}$$

where the total energy, E, is

$$E = E_{cm}+ E_v+ E_R \tag{3.25}$$

(3.23) into (3.24) and (3.25) gives

$$\begin{aligned} E_R\psi = -\frac{\hbar^2}{2M}\{&\frac{1}{r_o^2}\frac{\partial^2}{\partial\gamma^2} + 2(-\frac{1}{r_o}\frac{\sin\gamma}{\sin\beta}\frac{\partial}{\partial\alpha} - \frac{1}{r_o}\cos\gamma\frac{\partial}{\partial\beta} \\ &+ \frac{1}{r_o}\frac{\cos\beta\sin\gamma}{\sin\beta}\frac{\partial}{\partial\gamma})^2 \quad + \\ &\frac{3}{2}(-\frac{2}{\sqrt{3}r_o}\frac{\cos\gamma}{\sin\beta}\frac{\partial}{\partial\alpha} + \frac{2}{\sqrt{3}r_o}\sin\gamma\frac{\partial}{\partial\beta} + \frac{2}{\sqrt{3}r_o}\frac{\cos\beta\cos\gamma}{\sin\beta}\frac{\partial}{\partial\gamma})^2\}\psi \end{aligned} \tag{3.26}$$

$$E_R\psi = -\hbar^2\ \{\frac{1}{2[\frac{1}{2}Mr_o^2]}\frac{\partial^2}{\partial\beta^2} + \frac{1}{2[\frac{1}{2}Mr_o^2]}\cot\beta\frac{\partial}{\partial\beta} \quad +$$

$$+ \left(\frac{1}{2[Mr_o^2]} + \frac{\cot^2\beta}{2[\frac{1}{2}Mr_o^2]}\right) \frac{\partial^2}{\partial\gamma^2} + \frac{1}{2[\frac{1}{2}Mr_o^2]} \frac{1}{\sin^2\beta} \frac{\partial^2}{\partial\alpha^2}$$

$$- \frac{1}{2[\frac{1}{2}Mr_o^2]} \frac{2\cos\beta}{\sin^2\beta} \frac{\partial^2}{\partial\alpha\partial\gamma}\}\psi \tag{3.27}$$

(3.27) is the wave equation for a rigid rotor[4] of moments of inertia

$$I_x = I_y = \tfrac{1}{2}Mr_o^2$$

$$I_z = Mr_o^2$$

It has solutions

$$D^{\ell}_{mm'}(\alpha,\beta,\gamma) = \exp(-i\alpha m)d^{\ell}_{mm'}(\beta)\exp(-i\gamma m') \tag{3.28}$$

which are angular momentum eigenstates with eigenvalue equations

$$\begin{aligned} L^2\psi &= \ell(\ell+1)\hbar^2\psi \\ L_z\psi &= m\hbar\psi \end{aligned} \tag{3.29}$$

The $d^{\ell}_{mm'}(\beta)$ solve

$$\{\frac{d^2}{d\beta^2} + \cot\beta\frac{d}{d\beta} - \frac{m^2+m'^2-2mm'\cos\beta}{\sin^2\beta} + \ell(\ell+1)\}d^{\ell}_{mm'} = 0 \tag{3.30}$$

writing the remaining factor of $\psi$ as this $D^{\ell}_{mm'}$ and using (3.30), (3.27) becomes

$$E_R\psi = \{\ell(\ell+1) - \tfrac{1}{2}m'^2\} \frac{\hbar^2}{Mr_o^2} \tag{3.31}$$

Thus by changing the original variables from $(\underset{\sim}{r}_1, \underset{\sim}{r}_2, \underset{\sim}{r}_3)$ to the set $(\underset{\sim}{R}, \eta_1, \eta_2, \eta_3, \alpha, \beta, \gamma)$, $\psi$ is written as a product

$$\psi = \psi_{F.P.}(\underset{\sim}{R})\phi(\eta_1)\phi(\eta_2)\phi(\eta_3)D^{\ell}_{mm'}(\alpha,\beta,\gamma) \tag{3.32}$$

where $\psi_{F.P.}$ is the free particle wavefunction, $\phi$'s are harmonic oscillator wavefunctions, and $D^{\ell}_{mm'}$ is the rigid rotor wavefunction,[5] and by using the ground state harmonic oscillator wavefunction, we get the energy

$$(E-E_{cm}) = -3V_o + (1+\sqrt{2})\hbar\sqrt{\frac{3V''(r_o)}{4M}} + \{\ell(\ell+1) - \frac{m'^2}{2}\} \frac{\hbar^2}{Mr_o^2} \tag{3.33}$$

From (3.33) there is the following ordering of the rotational states. The $\ell=0$ state is the lowest; the $\ell=1$, $m'=1$ state is higher than $\ell=0$, but lower than the $\ell=1$, $m'=0$.

$$\begin{aligned} E_R(\ell=0) &= 0 \\ E_R(\ell=1,m'=1) &= \frac{3}{2}\frac{\hbar^2}{Mr_o^2} \\ E_R(\ell=1,m'=0) &= 2\frac{\hbar^2}{Mr_o^2} \end{aligned} \tag{3.34}$$

It should be remarked that (3.33) is not a systematic expansion in powers of $\hbar$. The first anharmonic corrections to the zero point vibration referred to following Eq. (3.16) are also of order $\hbar^2$.

# FOOTNOTES

1. G. Herzberg, Spectra of Diatomic Molecules, (Van Nostrand, Princeton, N.J., 1950).
2. L. W. Bruch and H. Stenschke, J. Chem. Phys. 57, 1019 (1972).
3. A. R. Edmonds, Angular Momentum in Quantum Mechanics, (Princeton, U.P., Princeton, N.J., 1960), p.66.
4. K. Gottfried, Quantum Mechanics, (Benjamin, N.Y., 1966), pp. 268-270, 276-278, 288.
5. Appendix A lists the $\ell=1$ rigid rotor wavefunctions.

# CHAPTER 4

# FERMION TRIMERS

We consider trimers composed of three identical spin one-half particles. As these are fermions and obey Fermi-Dirac statistics, the trimer wavefunctions must satisfy certain antisymmetry requirements. To incorporate spin, another factor is needed in the wavefunction; in the equilateral triangle model, this is in Eq. (3.32).

## A. Fermion Trimer Spin Structure

Intuitively, it is clear that there are two possible spin doublets of trimers of spin one-half particles. If all the spins align, the trimer has spin three-halves. If one of the spins is aligned opposite to the other two, then we have spin one-half (also referred to as the "mixed-symmetry") trimer.

To construct the trimer spin functions, we start with the spinor representation for each of the three particles, in which ↑ (and ↓) denotes eigenstates of the operators $S_i^2$ and $S_{iz}$ with eigenvalues $\frac{3}{4}\hbar^2$ and $\frac{1}{2}\hbar$ (and $\frac{3}{4}\hbar^2$ and $-\frac{1}{2}\hbar$). Spin operators for the trimer are formed by adding the single particle operators

$$S^2 = (S_1+S_2+S_3)^2$$
$$S_z = (S_{1z}+S_{2z}+S_{3z}) \qquad (4.1)$$

Spin functions for the trimer can then be formed as products of the single-particle spinors. Since there are two spin states per particle, there are eight independent three-particle spin states. To form an orthonormal set of eigenfunctions of the trimer spin operators, it is necessary to take combinations of the simple product states.

If $D^{\frac{1}{2}}$ denotes the single-particle spinor representation, then the representation of trimer spin states is the product representation:[1]

$$D^{\frac{1}{2}} \times D^{\frac{1}{2}} \times D^{\frac{1}{2}} = D^{\frac{1}{2}} \times (D^0+D^1)$$
$$= D^{\frac{1}{2}} + D^{\frac{1}{2}} + D^{3/2} \qquad (4.2)$$

From this we see that a set of spin states includes two doublets and a quartet giving

$2(2\times\frac{1}{2}+1) + (2\times\frac{3}{2}+1)=8$ independent spin states.

The quartet contains the four eigenstates of $S^2 = \frac{3}{2}\times\frac{5}{2}\hbar^2 : S_z = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}\,\hbar$ .

Each doublet contains two eigenstates of $S^2 = \frac{1}{2}\times\frac{3}{2}\hbar^2 : S_z = \frac{1}{2}, -\frac{1}{2}\,\hbar$ .

Denote the spin eigenstates of the trimer by $|s,m_s>$, where

$$\left.\begin{aligned} S^2|s,m_s\rangle &= s(s+1)\hbar^2|s,m_s\rangle \\ S_z|s,m_s\rangle &= m_s\hbar|s,m_s\rangle \end{aligned}\right. \qquad (4.3)$$

One of the possible ways of giving the eight spin eigenstates of the trimer is the set[2]

$$\left.\begin{aligned} \uparrow\uparrow\uparrow \quad &= |\tfrac{3}{2},\tfrac{3}{2}\rangle \\ \frac{1}{\sqrt{3}}(\uparrow\downarrow\uparrow+\downarrow\uparrow\uparrow+\uparrow\uparrow\downarrow) \quad &= |\tfrac{3}{2},\tfrac{1}{2}\rangle \\ \frac{1}{\sqrt{3}}(\downarrow\uparrow\downarrow+\uparrow\downarrow\downarrow+\downarrow\downarrow\uparrow) \quad &= |\tfrac{3}{2},-\tfrac{1}{2}\rangle \\ \downarrow\downarrow\downarrow \quad &= |\tfrac{3}{2},-\tfrac{3}{2}\rangle \end{aligned}\right\} \qquad (4.4)$$

$$\left.\begin{aligned} \frac{1}{\sqrt{6}}(2\uparrow\uparrow\downarrow-\uparrow\downarrow\uparrow-\downarrow\uparrow\uparrow) \quad &= |\tfrac{1}{2},\tfrac{1}{2}\rangle_s \\ \frac{1}{\sqrt{6}}(2\downarrow\downarrow\uparrow-\downarrow\uparrow\downarrow-\uparrow\downarrow\downarrow) \quad &= |\tfrac{1}{2},-\tfrac{1}{2}\rangle_s \end{aligned}\right\} \qquad (4.5)$$

$$\left.\begin{aligned} \frac{1}{\sqrt{2}}(\uparrow\downarrow\uparrow-\downarrow\uparrow\uparrow) \quad &= |\tfrac{1}{2},\tfrac{1}{2}\rangle_a \\ \frac{1}{\sqrt{2}}(\downarrow\uparrow\downarrow-\uparrow\downarrow\downarrow) \quad &= |\tfrac{1}{2},-\tfrac{1}{2}\rangle_a \end{aligned}\right\} \qquad (4.6)$$

(4.4) is the spin quartet; (4.5) and (4.6) are the two spin doublets.

For the spin $|\frac{1}{2}, \pm\frac{1}{2}>$ states, i.e., for the spin $\frac{1}{2}$ trimer, there are two doublets to contribute to the wavefunction; one is symmetric and the other is antisymmetric under interchange of particles one and two.

B. Three-Particle Exchange

The set of three-particle exchanges consists of three pair exchange, two cyclic exchanges, and the identity. This set forms a mathematical group, the permutation group of three objects. A permutation can be specified by the symbol

$$\begin{pmatrix} 1 & 2 & 3 \\ \alpha_1 & \alpha_2 & \alpha_3 \end{pmatrix} \tag{4.7}$$

where the $\alpha_i$ are a rearrangement of 1,2,3. The permutation represented is the one where each number in the upper line is replaced by the number below it on the lower line. In this notation, the triangle symmetry group operations are given below in (4.8)

$$E = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \end{pmatrix}, \quad A = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 1 & 3 \end{pmatrix}, \quad B = \begin{pmatrix} 1 & 2 & 3 \\ 1 & 3 & 2 \end{pmatrix}$$

$$C = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 2 & 1 \end{pmatrix} \quad D = \begin{pmatrix} 1 & 2 & 3 \\ 3 & 1 & 2 \end{pmatrix} \quad F = \begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 1 \end{pmatrix} \tag{4.8}$$

This group has the multiplication table (4.9)

| | E | A | B | C | D | F |
|---|---|---|---|---|---|---|
| E | E | A | B | C | D | F |
| A | A | E | D | F | B | C |
| B | B | F | E | D | C | A |
| C | C | D | F | E | A | B |
| D | D | C | A | B | F | E |
| F | F | B | C | A | E | D |

(4.9)

Another notation often used for these permutations is

$$P_{12} = A, \quad P_{23} = B, \quad P_{31} = C$$
$$C_{123} = D, \quad C'_{123} = F \qquad (4.10)$$

## C. Exchange Restrictions on the Fermion Trimer Wavefunction

### 1. General form of wavefunction

Operations A,B,C are pair exchanges; as such, when operating on the fermion trimer wavefunction, they must take it to minus itself. D and F are three-cycle exchanges and correspond by (4.9) to two pair-exchanges; thus these operations must leave the trimer wavefunction invariant.

The Hamiltonian, the angular momentum operators, and the spin operators (4.3) all commute, so that simultaneous eigenstates are possible. The wavefunction is written as a product of a spin part and a spatial part which includes the rotational eigenstates. A wavefunction in the form (3.32) is not possible in general for a non-rigid body, where the body-fixed z-component of angular momentum is not a good quantum number. Apart from the free particle motion of the center of mass, the wavefunction (for each spin state $\chi$),

$$\begin{aligned} \psi &= \phi^{\ell}_{m}\,\chi \\ \phi^{\ell}_{m} &= \sum_{m'=-\ell}^{\ell} g^{\ell}_{m'}\, D^{\ell}_{mm'} \end{aligned} \qquad (4.11)$$

where $g^{\ell}_{m'}$ depends only on the internalrelative coordinates of the three particles. $\chi$ is the spin part, and the $D^{\ell}_{mm'}$ are the symmetric top wavefunctions discussed in (3.28). These $D^{\ell}_{mm'}$ 's serve here as a complete set of $\ell,m$ eigenstates.

## 2. Parity eigenstates

As we will discuss later in Section D, the permutations of the three particles can be understood as proper rotations. There is a distinct operation,[3] space-inversion, which also leaves the Hamiltonian invariant.

Spin is an angular momentum, and as such is a pseudovector unaffected by an inversion, therefore it is sufficient to look only at the spatial part of the wavefunction in imposing the symmetry under inversion.

We require that $\psi$ in (4.11) be a parity eigenstate, i.e., $P\psi=\pm\psi$. The effect of the parity operation is only on the Euler angles, as the interparticle coordinates are unaffected. The effect is that of rotating the triangle by $\pi$ about the body-fixed z-axis. This means increasing the Euler angle $\gamma$ by $\pi$.[4]

$$\begin{aligned} PD^{\ell}_{mm'}(\alpha,\beta,\gamma) &= D^{\ell}_{mm'}(\alpha,\beta,\gamma+\pi) \\ &= e^{im'\pi}\, D^{\ell}_{mm'}(\alpha,\beta,\gamma) \qquad (4.12) \\ &= (-1)^{m'}\, D^{\ell}_{mm'}(\alpha,\beta,\gamma) \end{aligned}$$

The requirement that $\psi$ in (4.11) is a parity eigenstate means that only exclusively even or odd $m'$ can contribute to $\psi$.

### 3. Exchange restrictions on spin-$\frac{3}{2}$ trimer eigenstates

For the spin-$\frac{3}{2}$ trimer, eigenstates of the spin quartet (4.4) are symmetric under all interchanges and therefore are invariant under the group operations. In the product representation the group acts only on $\phi^{\ell}_{m}$ (4.11).

The $\ell=0$ rotational eigenstate $D^0_{00}=1$ is excluded because it is invariant under all exchange operations

For $\ell=1$, from (4.11)

$$\phi_m = g^1_1 D^1_{m1} + g^1_o D^1_{mo} + g^1_{-1} D^1_{m-1} \tag{4.13}$$

Because $\phi^1_m$ must be a parity eigenstate $g^1_o$ and the $g^1_{\pm 1}$ cannot both contribute. We will be guided in choosing $g^1_{\pm 1}=0$ in a later section.

## 4. Exchange restrictions in spin-$\frac{1}{2}$ trimer eigenstates

For the mixed-symmetry trimer, there are two spin doublets (4.5) and (4.6) from which $\psi$ is constructed. The doublet $\chi_s$ in (4.5) is symmetric under the exchange of particles one and two; the doublet $\chi_a$ in (4.6) is antisymmetric under this pair exchange.

$$\psi = \phi_a \chi_s + \phi_s \chi_a \tag{4.14}$$

$\phi_a$ and $\phi_s$ are antisymmetric and symmetric, respectively, under the pair exchange of one and two, so that $\psi$ is antisymmetric overall.

Consider the $|\frac{1}{2},\frac{1}{2}>$ case. The same relations also hold for $|\frac{1}{2},-\frac{1}{2}>$.

$$\begin{aligned} \chi_s &= \frac{1}{\sqrt{6}}(2\uparrow\uparrow\downarrow - \uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow) \\ \chi_a &= \frac{1}{\sqrt{2}}(\uparrow\downarrow\uparrow - \downarrow\uparrow\uparrow) \end{aligned} \tag{4.15}$$

We consider the pair exchange A and the cyclic exchange D which are sufficient to generate the permutation group.

$$\begin{aligned} A\,\chi_s &= \chi_s \\ D\,\chi_s &= -\tfrac{1}{2}\chi_s + \tfrac{\sqrt{3}}{2}\chi_a \end{aligned} \tag{4.16}$$

$$\begin{aligned} A\,\chi_a &= -\chi_a \\ D\,\chi_a &= -\tfrac{\sqrt{3}}{2}\chi_s - \tfrac{1}{2}\chi_a \end{aligned} \tag{4.17}$$

Requiring $\psi$ be antisymmetric under A and symmetric under D, (4.14), (4.16), and (4.17) allow us to deduce that

$$\begin{aligned} A\psi &= -\psi = (A\phi_a)\chi_s - (A\phi_s)\chi_a \\ D\psi &= [-\tfrac{1}{2}(D\phi_a) - \tfrac{\sqrt{3}}{2}(D\phi_s)]\chi_s \\ &\quad + [\tfrac{\sqrt{3}}{2}(D\phi_a) - \tfrac{1}{2}(D\phi_s)]\chi_a \end{aligned} \tag{4.18}$$

and that

$$\begin{aligned} A\phi_a &= -\phi_a \\ D\phi_a &= -\tfrac{1}{2}\phi_a + \tfrac{\sqrt{3}}{2}\phi_s \end{aligned} \tag{4.19}$$

$$\begin{aligned} A\phi_s &= \phi_s \\ D\phi_s &= -\tfrac{\sqrt{3}}{2}\phi_a - \tfrac{1}{2}\phi_s \end{aligned} \tag{4.20}$$

$\phi_a$ and $\phi_s$ are expanded in rotational eigenstates

$$\begin{aligned} \phi_a &= b_1\, D^1_{m_1} + b_o\, D^1_{m_o} + b_{-1}\, D^1_{m-1} \\ \phi_s &= a_1\, D^1_{m_1} + a_o\, D^1_{m_o} + a_{-1}\, D^1_{m-1} \end{aligned} \tag{4.21}$$

where the $a_i$ and $b_i$ are functions of the internal coordinates. We do not assume that they are symmetric, but allow them to change under interchanges. As in the previous section we cannot have both even and odd parity states contributing. Guidance in the choice will be provided later, where we will see that $b_o=a_o=0$. From this we will be able to conclude that $\phi_a$ and $\phi_s$ are each made up of $D^1_{m1}$ and $D^1_{m-1}$.

## D. Equilateral Triangle Case

### 1. Exchange group

The case of the equilateral triangle provides guidance for the more general case, because it can be systematically solved in terms of the group of covering operations on the triangle.[5]

This group consists of five operations, labelled A,B,C,D,F in addition to the identity E. A,B,C are rotations by $\pi$ about the body-fixed axes in the plane of the triangle as is shown in Fig. 4-1. D is a clockwise rotation by $\frac{2\pi}{3}$ in the plane of the triangle, and F is a clockwise rotation by $\frac{4\pi}{3}$ in the same plane.

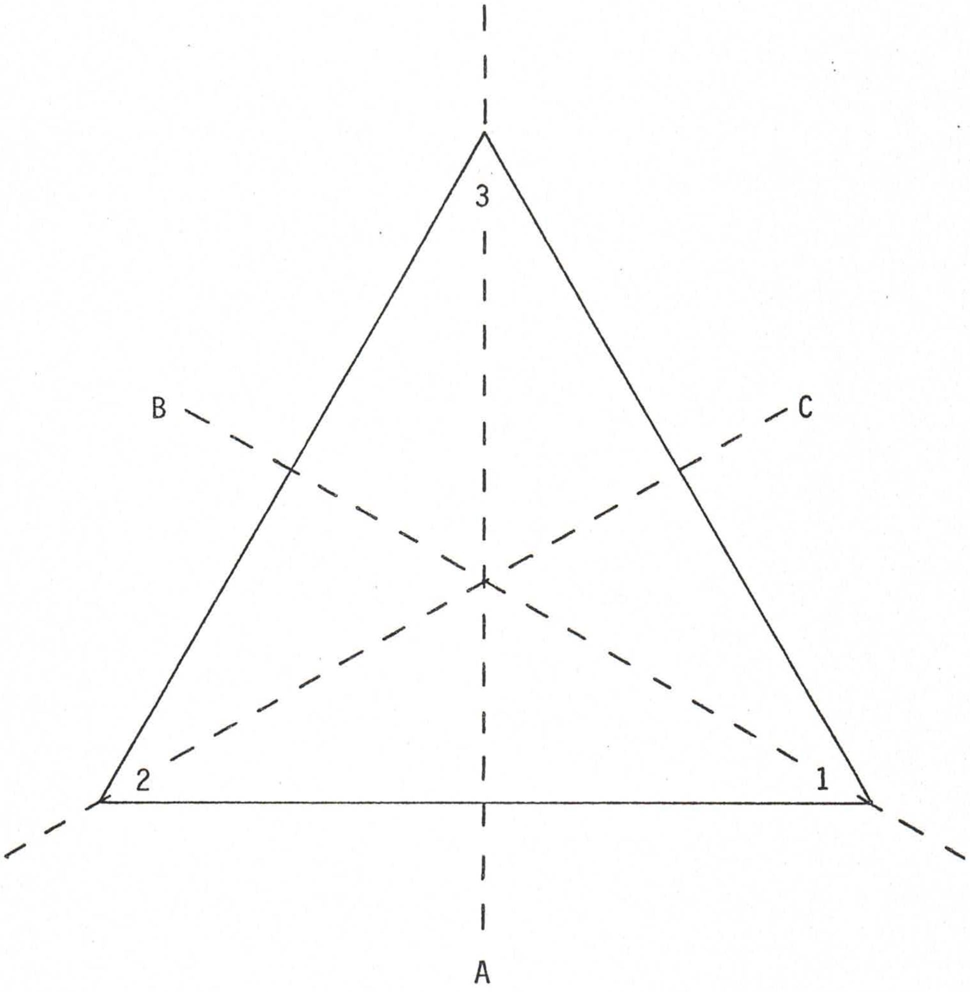

Figure 4-1

This group of covering operations has the multiplication table (4.9) and the representation (4.8).

Another representation of this group is provided by the $(2\ell+1)$-dimensional matrices

$$D^{\ell}_{mm'}(\alpha,\beta,\gamma)$$

The group operations in this representation are

$$\begin{aligned}
E &= D^{\ell}_{mm'}(0,0,0) = \delta_{mm'} \\
A &= D^{\ell}_{mm'}(0,-\pi,0) = (-1)^{\ell+m}\ \delta_{-mm'} \\
B &= D^{\ell}_{mm'}(-\tfrac{\pi}{3},-\pi,\tfrac{\pi}{3}) = (-)^{\ell+m}\ e^{im\frac{2\pi}{3}}\ \delta_{-m,m'} \\
C &= D^{\ell}_{mm'}(\tfrac{\pi}{3},-\pi,-\tfrac{\pi}{3}) = (-1)^{\ell+m}\ e^{-im\frac{2\pi}{3}}\ \delta_{-m,m'} \\
D &= D^{\ell}_{mm'}(-\tfrac{2\pi}{3},0,0) = e^{im\frac{2\pi}{3}}\ \delta_{mm'} \\
F &= D^{\ell}_{mm'}(\tfrac{2\pi}{3},0,0) = e^{-im\frac{2\pi}{3}}\ \delta_{mm'}
\end{aligned} \tag{4.22}$$

If G is one of the operations in (4.22), its effect on a rotational eigenstate in (4.11) is

$$G\ \phi^{\ell}_{m} = \sum_{\substack{m'' \\ m'}} g^{\ell}_{m'}\ D^{\ell}_{mm''}(\alpha,\beta,\gamma)\ G_{m''m'} \tag{4.23}$$

### 2. Further exchange restrictions on spin-$\frac{3}{2}$ trimer

Applying A from (4.22) on $\phi^{1}_{m}$ in (4.13) by (4.23) we see that

$$g_1^1 = -g_{-1}^1 \tag{4.24}$$

Applying B from (4.22) the same way, we get

$$g_1^1 \, e^{i\frac{2\pi}{3}} = -g_{-1}^1 \tag{4.25}$$

together (4.24) and (4.25) imply that

$$g_1^1 = g_{-1}^1 = 0 \tag{4.26}$$

so only the $D'_{m_o}$ term in (4.13) contributes, and the ground state of the spin-$\frac{3}{2}$ trimer for the equilateral triangle is

$$\phi_m^1 = g^1 \, D_m^1 \, (\alpha,\beta,\gamma) \tag{4.27}$$

## 3. Further exchange restrictions on spin-$\frac{1}{2}$ trimer

Applying operation A from (4.22) on $\phi_a$ in (4.21) by (4.23), using (4.19):

$$\begin{aligned} A\, b_1 &= -b_{-1} \\ A\, b_o &= b_o \\ A\, b_{-1} &= -b_1 \end{aligned} \tag{4.28}$$

Likewise in $\phi_s$, using (4.20)

$$\begin{aligned} A\, a_1 &= a_{-1} \\ A\, a_o &= -a_o \\ A\, a_{-1} &= a_1 \end{aligned} \tag{4.29}$$

B and D on $\phi_a$ and $\phi_s$, treated similarly, give a set of relations that, combined with (4.28) and (4.29) together with the relation AB=D from the multiplication table (4.9), allow us to conclude

$$\begin{aligned} b_1 &= -i\, a_1 \\ a_o &= b_o = 0 \\ b_{-1} &= i\, a_{-1} \end{aligned} \tag{4.30}$$

(4.30) into (4.21) gives

$$\begin{aligned} \phi_a &= (-ia_1)D^1_{m1} + (ia_{-1})D^1_{m-1} \\ \phi_s &= a_1 D^1_{m1} + a_{-1}D^1_{m-1} \end{aligned} \tag{4.31}$$

so that for the equilateral triangle

$$\psi=[(-ia_1)D^1_{m1} + (ia_{-1})D^1_{m-1}]\chi_s + [a_1 D^1_{m1} + a_{-1}D^1_{m-1}]\chi_a \tag{4.32}$$

# FOOTNOTES

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5. M. Tinkham, op. cit., Chapter 1.

# CHAPTER 5

# VARIATIONAL METHOD FOR THE BOSON TRIMER

Variational methods have been used successfully to bound boson trimer ground state energies.[1] In this chapter we consider a loosely bound trimer of three spinless particles in three dimensions. Because of the exchange symmetry of bosons, the ground state has angular momentum $\ell=0$. This leads to a considerable simplification in the Schroedinger equation (3.1) when it is written in terms of the interparticle coordinates.

Four potentials are considered: the square well, the exponential, the Yukawa, and the Gaussian. A variational calculation is made for each using the Jastrow trial function and a numerical determination is made of the minimum necessary potential attraction for the trimer to be bound. A comparison of this bound on the potential with a bound from the known two-body case shows that our treatment gives a more restrictive upper bound.

## A. Interparticle Coordinates

We introduce the inter-particle coordinates

$$\begin{aligned} r &= |\underset{\sim}{r}_{31}| = |\underset{\sim}{r}_3-\underset{\sim}{r}_1| \\ s &= |\underset{\sim}{r}_{23}| = |\underset{\sim}{r}_2-\underset{\sim}{r}_3| \\ t &= |\underset{\sim}{r}_{12}| = |\underset{\sim}{r}_1-\underset{\sim}{r}_2| \end{aligned} \qquad (5.1)$$

The potential in (3.1) is assumed to be due to pair-potentials $V(r_{ij})$ which depend only on the interparticle separations.

$$\begin{aligned} V(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) &= V(|\underset{\sim}{r}_3-\underset{\sim}{r}_1|,\ |\underset{\sim}{r}_2-\underset{\sim}{r}_3|,\ |\underset{\sim}{r}_1-\underset{\sim}{r}_2|) \\ &= V(r,s,t) \qquad (5.2) \\ &= V(r)+V(s)+V(t) \end{aligned}$$

To integrate over the three-particle volume, it is sufficient to integrate over the two particle positions $\underset{\sim}{r}_{31}$, $\underset{\sim}{r}_{23}$ including the orientation angle $\theta$ between $\underset{\sim}{r}_{31}$ and $\underset{\sim}{r}_{23}$, since these specify the positions of all three particles. This volume integral has the form

$$\int_{r=0}^{\infty} \int_{s=0}^{\infty} \int_{-1}^{1} r^2 dr\ s^2 ds\ d(\cos\theta) \qquad (5.3)$$

The law of cosines $t^2=r^2+s^2-2rs\cos\theta$ for the triangle defined by (5.1) gives

$$rs d(\cos\theta) = t\ dt \qquad (5.4)$$

and $t=|r-s|$ when $\cos\theta=1$, and $t=r+s$, when $\cos\theta=-1$. Putting this into (5.3), the volume integral is

$$\int_{r=0}^{\infty} \int_{s=0}^{\infty} \int_{t=|r-s|}^{r+s} rst \; drdsdt \qquad (5.5)$$

(5.4) has a symmetric form that is valuable in computing volume integrals.

### B. Trial Wavefunction

In the variational method, an intelligent guess is made about the ground state wavefunction, which is written in terms of an adjustable parameter. The variational energy of this system is calculated as a function of this parameter. This energy is then minimized over the parameter and the result serves as an upper bound to the exact energy of the system.

The wavefunction is chosen to be a symmetric function of the interparticle coordinates. Evidence[2] indicates that the Jastrow trial function is a reasonable choice near threshold binding since it gets the correct form of the wavefunction at large distances.

$$g(r,s,t) = N \, e^{-\alpha(r+s+t)} \qquad (5.6)$$

Using volume integral (5.5) to compute the normalization N,

$$\int_0^{\infty} \int_0^{\infty} \int_{|r-s|}^{r+s} g^2 \, rst \; drdsdt = 1 = N^2 \int\!\!\int\!\!\int e^{-2\alpha(r+s+t)} rst \; drdsdt$$

$$= N^2 \frac{7}{2^{10}\alpha^6}$$

which gives

$$N = \frac{2^5\alpha^3}{\sqrt{7}} \qquad (5.7)$$

C. Kinetic Energy

The kinetic energy[3] is calculated in rectangular coordinates from (5.6) using the operator

$$(\text{K.E.}) = -\frac{\hbar^2}{2M}(\nabla_1^2+\nabla_2^2+\nabla_3^2) \qquad (5.8)$$

(5.8) on (5.6) gives

$$(\text{K.E.})g = -\frac{\hbar^2}{2M}\, 6\alpha^2 + \alpha^2\left(\frac{r^2t+s^2t-t^3+rs^2+rt^2-r^3+st^2+r^2s-s^3}{rst}\right)$$

$$- 4\alpha\left(\frac{1}{r}+\frac{1}{s}+\frac{1}{t}\right)\} \qquad (5.9)$$

The expectation value of the kinetic energy is

$$<\text{K.E.}> = \iiint g(\text{K.E.})g \; rstdrdsdt$$

$$= -\frac{\hbar^2}{2M}\cdot\frac{2^{10}\alpha^6}{7}\int_0^\infty\int_0^\infty\int_{|r-s|}^{r+s} \{6\alpha^2+\alpha^2\left(\frac{r^2t+s^2t-t^3+rs^2+rt^2-r^3+st^2+r^2s-s^3}{rst}\right)$$

$$(5.10)$$

$$-4\alpha\left(\frac{1}{r}+\frac{1}{s}+\frac{1}{t}\right)\} \; e^{-2\alpha(r+s+t)} \; rstdrdsdt$$

Doing the integrals in (5.10) is straightforward. The values of integrals needed are tabulated in Appendix B. The result is

$$\langle K.E.\rangle = \frac{30}{7}\frac{\hbar^2\alpha^2}{M} \tag{5.11}$$

## D. Models

We will now consider four potentials, the square well, the exponential, the yukawa, and the gaussian. For each we calculate the variational energy and from this we determine an upper bound to the binding parameter at threshold.

### 1. Square well potential

In (5.2) we use the pair-potential

$$V(r_{ij}) = \begin{cases} -V_o, & r_{ij} < r_o \\ 0, & \text{otherwise} \end{cases} \tag{5.12}$$

The expectation value of the potential energy,

$$\langle V(r,s,t)\rangle = \iiint gV(r,s,t)g\ rst\ drdsdt \tag{5.13}$$

with g from (5.6), (5.13) gives

$$\begin{aligned}\langle V(r,s,t)\rangle &= \frac{2^{10}\alpha^6}{7}\iiint (V(r)+V(s)+V(t))rste^{-2\alpha(r+s+t)}drdsdt \\ &= \frac{2^{10}\alpha^6}{7}3\iiint V(r)rste^{-2\alpha(r+s+t)}drdsdt \qquad (5.14) \\ &= -\frac{2^{10}\alpha^6}{7}3V_o\int_{r=0}\int_{s=0}^{\infty}\int_{t=|r-s|}^{r+s} rste^{-2\alpha(r+s+t)}drdsdt \\ &= -3V_o\{1-[\frac{(4\alpha r_o)^4}{84}+\frac{5(4\alpha r_o)^3}{42}+\frac{(4\alpha r_o)^2}{2}+(4\alpha r_o)+1]e^{-4\alpha r_o}\}\end{aligned}$$

Introducing the dimensionless parameters

$$x = 4\alpha r_o \qquad K = \frac{Mr_o^2V_o}{\hbar^2} \tag{5.15}$$

x is the variational parameter and K is the binding parameter. Combining (5.11) and (5.14) with (5.15), we get the equation:

$$\left(\frac{E}{3V_o}\right) = \frac{5}{56}\frac{x^2}{K} - 1 + \left[\frac{x^4}{84} + \frac{5x^3}{42} + \frac{x^2}{2} + x + 1\right]e^{-x} \tag{5.16}$$

Using a programmable calculator, the variation over x in (5.16) has been studied numerically as a function of K.

Figure 5-1 shows $\frac{E}{3V_o}$ as a function of variational parameter x, formula (5.16), for three values of K. The top figure shows that when K=2, the minimum in the graph has positive energy, hence the trimer is not bound. The bottom figure has K=2.15; the energy at the minimum is negative and the system is bound. The center graph corresponds to K=2.096023, which gives threshold binding for wavefunction (5.6).

$$K_c^{ub} = 2.096023 \tag{5.17}$$

Because our variational energy (5.16) is an upper bound to the exact energy for the potential considered,

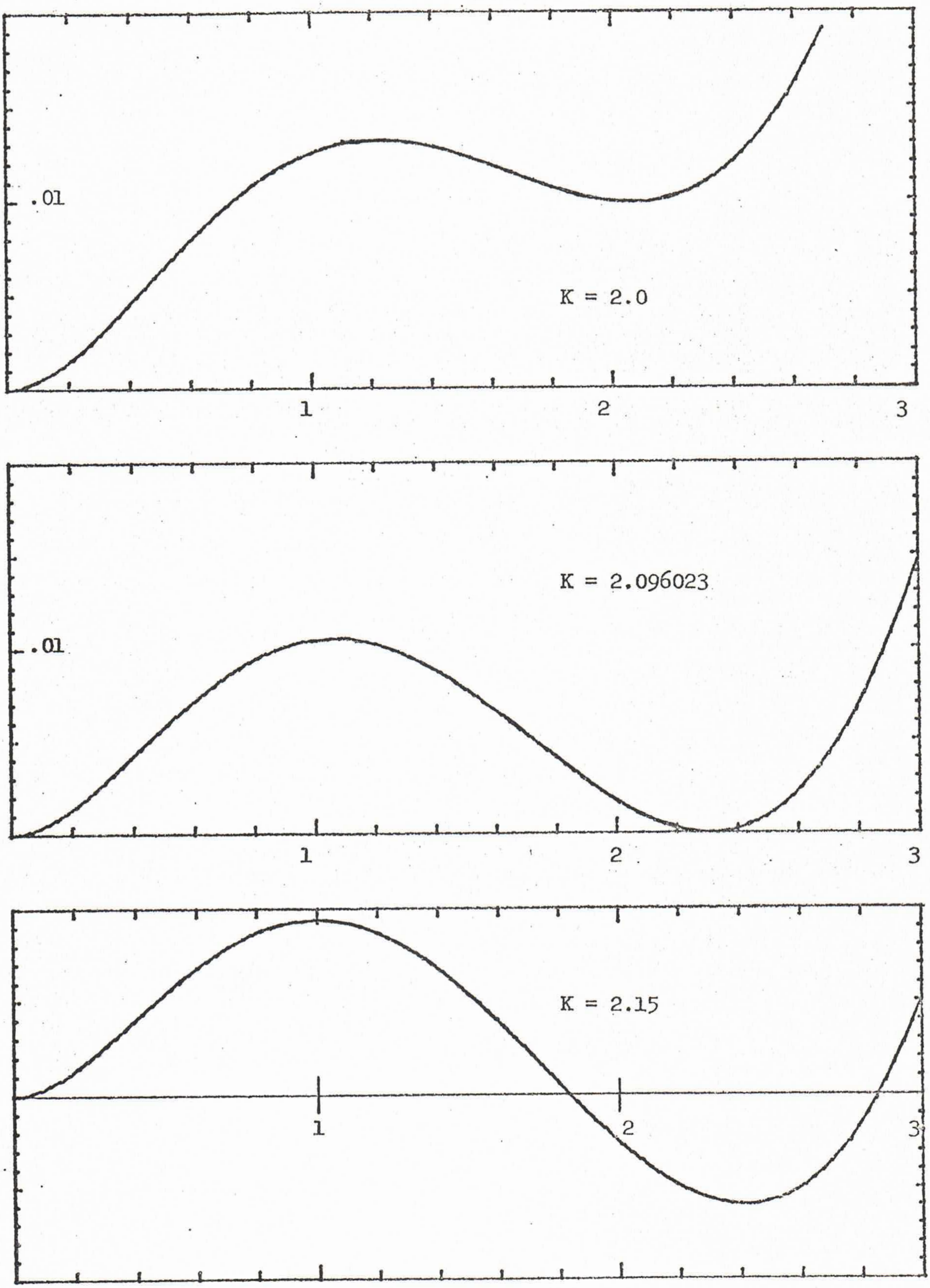

Figure 5-1 Boson Trimer Variational Energy, Square Well Potential

(5.17) is an upper bound on the exact threshold binding parameter for the square well.

A comparison is now possible between (5.17) and the corresponding binding parameter in the two-body problem. Using the Hall-Post lower bound[4] and the Bruch-Sawada upper bound[5] in the trimer ground state energies we know that the three-body threshold binding parameter lies between $\frac{2}{3}$ of the two-body parameter and the two-body value[6] is $\pi^2/4 = 2.467401$, thus

$$\frac{2}{3}\,\frac{\pi^2}{4} = 1.644934 \leq K_c \leq K_c{}^b = 2.096023 < 2.467401 \qquad (5.18)$$

From (5.18) we see that we have considerably improved the upper bound on $K_c$ using (5.1-).

### 2. Exponential potential

As in Section 5, with the pair-potential

$$V(r_{ij}) = -V_o e^{-r_{ij}/r_o} \qquad (5.19)$$

we get

$$\langle V(r,s,t)\rangle = \frac{2^{10}\alpha^6}{7}\iiint \left[-V_o e^{-\frac{r}{r_o}} - V_o e^{-\frac{s}{r_o}} - V_o e^{-\frac{t}{r_o}}\right] rst \qquad (5.20)$$

$$\times \; e^{-2\alpha(r+s+t)}\,drdsdt$$

Use the dimensionless parameters (5.15), add (5.11) to (5.20) to get the energy

$$\frac{E}{3V_o} = \frac{5}{56}\frac{x^2}{K} - [\frac{2}{7}\frac{x^5}{(1+x)^5} + \frac{3}{7}\frac{x^4}{(1+x)^4} + \frac{2}{7}\frac{x^3}{(1+x)^3}] \qquad (5.21)$$

Numerical analysis of (5.21) yields threshold binding at

$$K_c^{ub} = 1.222041 \qquad (5.22)$$

The corresponding $K_c$ in the two-body problem is found by the tabulated zeros of the Bessel function, in the exact solution to the reduced Schroedinger equation, to be 1.446. This gives the bounds on the three body threshold binding parameter $K_c$:

$$\frac{2}{3}(1.446) = .964 \leq K_c \leq K^{ub} = 1.222041 < 1.446 \qquad (5.23)$$

From (5.23) we see that (5.22) is a considerably improved upper bound.

### 3. Yukawa potential

We proceed as before using the pair-potential

$$V(r_{ij}) = -V_o \frac{r_o}{r_{ij}} e^{-r_{ij}/r_o} \qquad (5.24)$$

$$\langle V(r,s,t)\rangle = -V_o \frac{3}{7}[\frac{1}{2}\frac{(4\alpha r_o)^5}{(1+4\alpha r_o)^4} + \frac{(4\alpha r_o)^4}{(1+4\alpha r_o)^3} + \frac{(4\alpha r_o)^3}{(1+4\alpha r_o)^2}] \qquad (5.25)$$

By (5.15), (5.11), and (5.25)

$$\frac{E}{3V_o} = \frac{5}{56}\frac{x^2}{K} - \left[\frac{x^5}{14(1+x)^4} + \frac{x^4}{7(1+x)^3} + \frac{x^3}{7(1+x)^2}\right] \qquad (5.26)$$

Numerical analysis of (5.26) yields threshold binding at

$$K_c^{ub} = 1.462678 \qquad (5.27)$$

We use the Hulthen and Laurikainen[7] result for the two-body problem, 1.679816, and compare.

$$\tfrac{2}{3}(1.679816) = 1.1198773 \le K_c \le K_c^{ub} = 1.4626781 < 1.679816 \qquad (5.28)$$

From (5.28) we see that (5.27) improves the upper bound on $K_c$.

## 4. Gaussian potential

We proceed as previously, with the pair-potential

$$V(r_{ij}) = -V_o\, e^{-r_{ij}^2/r_o^2} \qquad (5.29)$$

we use the dimensionless variational parameter

$$\gamma = 2\alpha r_o = \frac{x}{2} \qquad (5.30)$$

$$\langle V(r,s,t)\rangle = -3V_o\{-\tfrac{4}{21}\gamma^8 + \tfrac{2}{21}\gamma^6 + [\tfrac{4}{21}\gamma^9 - \tfrac{1}{7}\gamma^5 + \tfrac{2}{7}\gamma^3]\sqrt{\pi}\, e^{\gamma^2} \times [1-\mathrm{erf}(\gamma)]\} \qquad (5.31)$$

where erf($\Upsilon$) is the "error function".

$$\mathrm{erf}(\Upsilon) \equiv \frac{2}{\sqrt{\pi}} \int_0^{\Upsilon} e^{-t^2}\, dt \tag{5.32}$$

By (5.31), with (5.11), (5.15), and (5.30)

$$\frac{E}{3V_o} = \frac{5}{14}\,\frac{\gamma^2}{K} - \{-\frac{4}{21}\gamma^8 + \frac{2}{21}\gamma^6 + [\frac{4}{21}\gamma^9 - \frac{1}{7}\gamma^5 + \frac{2}{7}\gamma^3]\sqrt{\pi}e^{\gamma^2}[1-\mathrm{erf}(\gamma)] \tag{5.33}$$

A numerical analysis is done using a numerical approximation[8] for the error function, with the result

$$K_c^{ub} = 2.247772 \tag{5.34}$$

The two body result is obtained by numerical integration to be 2.684.

$$\frac{2}{3}(2.684) = 1.789 \le K_c \le K_c^{ub} = 2.247772 < 2.684 \tag{5.35}$$

From (5.35), we see that (5.34) improves the upper bound.

# FOOTNOTES

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# CHAPTER 6

# VARIATIONAL METHOD FOR THE FERMION TRIMERS

In the rigid trimer model of Chapter 3 and in the exchange discussion of Chapter 4, we saw that the ground state of each of the fermion trimers has angular momentum $\ell=1$.

In Chapter 5, we used a form of the Jastrow trial function and found that it was easy to work with and that it gave good results.

In this chapter we construct trial wavefunctions for the spin-$\frac{1}{2}$ and spin-$\frac{3}{2}$ trimers. We require that these trial wavefunctions (i) meet the exchange symmetrization requirements; (ii) reflect the angular momentum quantum numbers; and (iii) incorporate much of the simplicity of the boson trial function.

These trial functions are then used in variational calculations for the same pair-potential models as in the previous chapter. Numerical upper bounds are given for the threshold binding parameters.

## A. Coordinate Relations

To proceed with the simplest equations, we use rectangular space-fixed coordinates to construct the wavefunctions and to calculate their kinetic energies. These coordinates are related to internal coordinates and the Euler angles by a set of relations[1] (6.1) below.

$$\begin{aligned} x_i &= (\cos\alpha\cos\beta\cos\gamma-\sin\alpha\sin\gamma)\xi_i \\ &\quad -(\cos\alpha\cos\beta\sin\gamma+\sin\alpha\cos\gamma)\eta_i+(\cos\alpha\sin\beta)\zeta_i \\ y_i &= (\sin\alpha\cos\beta\cos\gamma+\cos\alpha\sin\gamma)\xi_i \\ &\quad -(\sin\alpha\cos\beta\sin\gamma-\cos\alpha\cos\gamma)\eta_i+(\sin\alpha\sin\beta)\zeta_i \\ z_i &= -(\sin\beta\cos\gamma)\xi_i+(\sin\beta\sin\gamma)\eta_i+\cos\beta\zeta_i \end{aligned} \tag{6.1}$$

Our choice of body-fixed axes involves letting the trimer lie in the $\xi$-$\eta$ plane with the center of mass at the origin. These conditions are

$$\zeta_1 = \zeta_2 = \zeta_3 = 0 \tag{6.2}$$

$$\xi_1 + \xi_2 + \xi_3 = \eta_1 + \eta_2 + \eta_3 = 0$$

It will be useful to note that from the form of the $\ell=1$ rigid rotor wavefunction,[2]

$$\begin{aligned} D^1_{00} &= \cos\beta \\ \frac{D^1_{01}-D^1_{0-1}}{\sqrt{2}} &= \sin\beta\cos\gamma \\ \frac{D^1_{01}+D^1_{0-1}}{\sqrt{2}\,i} &= \sin\beta\sin\gamma \end{aligned} \tag{6.3}$$

Exchange constraints are imposed by using the antisymmetrizer,

$$\text{Antisymmetrizer} = \tfrac{1}{6}(1-P_{12}-P_{23}-P_{31}+C_{123}+C'_{123}) \qquad (6.4)$$

where $P_{ij}$ is a pair-exchange of particles i and j, $C_{123}$ and $C'_{123}$ are the two three-cycle exchanges as discussed in (4.10).

## B. Spin-$\frac{1}{2}$ Trimer (Mixed-Symmetry Trimer)

### 1. Spin-$\frac{1}{2}$ trial wavefunction

A direct way of meeting the requirements stated in Section A.1 is to multiply the boson trial wavefunction (5.6) by a function of the particle coordinates.

For the mixed-symmetry trimer, the form of the wavefunction is given in Eq. (4.18)

$$\psi = \phi_a \chi_s + \phi_s \chi_a \qquad (6.5)$$

Guidance in constructing $\phi_a$ and $\phi_s$ is provided by the exactly soluble case of the pair potential

$$V(r_{ij}) = \tfrac{1}{2}k\ r_{ij}^2$$

We construct $\phi_a$ and $\phi_s$ by multiplying (5.6) by a linear function of the inter-particle coordinates. There is some arbitrariness in this choice, reflecting the degeneracy of the space quantization of non-zero angular momenta. $\phi_a$ must be antisymmetric under the interchange of particles one and two.

$$\phi_a = N(z_1-z_2)e^{-\alpha(r_{12}+r_{23}+r_{21})} \qquad (6.6)$$

$\phi_s$ must be symmetric under the interchange of particles one and two.

$$\phi_s = N\frac{1}{\sqrt{3}}[(z_3-z_1)-(z_2-z_3)]e^{-\alpha(r_{12}+r_{23}+r_{31})} \qquad (6.7)$$

Putting (6.5), (6.6), and (6.7) together

$$\psi = N\{(z_1-z_2)e^{-\alpha(r_{12}+r_{23}+r_{31})}\chi_s \qquad (6.8)$$

$$+ \frac{2}{\sqrt{3}}[z_3-\tfrac{1}{2}(z_1+z_2)e^{-\alpha(r_{12}+r_{23}+r_{31})}\chi_a\}$$

$P_{12}\psi = -\psi$ is automatic and $C_{123}\psi = \psi$ is readily verified. Combining (6.1), (6.2), and (6.3) with (6.8)

$$\psi = N\{\frac{1}{\sqrt{2}}([-(\xi_1-\xi_2)-i(\eta_1-\eta_2)]D^1_{01}+[(\xi_1-\xi_2)-i(\eta_1-\eta_2)]D^1_{0-1})$$

$$\times\ e^{-\alpha(r_{12}+r_{23}+r_{31})}\ \chi_s \qquad (6.9)$$

$$+ \sqrt{\tfrac{2}{3}}([-(\xi_3-\xi_1)+(\xi_2-\xi_3)-i(\eta_3-\eta_1)+i(\eta_2-\eta_3)]D^1_{01}$$

$$+ \ [(\xi_3-\xi_1)-(\xi_2-\xi_3)-i(\eta_3-\eta_1)+i(\eta_2-\eta_3)]D^1_{0-1})$$

$$\times\ e^{-\alpha(r_{12}+r_{23}+r_{31})}\ \chi_a\}$$

This is consistent with the arguments of Section 6 of Chapter 4.

In terms of the volume integral discussed in Section A.2 of the previous chapter, the normalization N for $\psi$ when integrating over two vector interparticle coordinates is

$$N = \frac{(2\alpha)^4}{(2\pi)\sqrt{3}} \tag{6.10}$$

## 2. Spin-$\frac{1}{2}$ kinetic energy

In rectangular coordinates, the trimer kinetic energy operator is

$$-\frac{\hbar^2}{2M}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) \tag{6.11}$$

(6.11) on (6.8) gives

$$\begin{aligned}
&-\frac{N\hbar^2}{2M}(2\alpha[\frac{-2(z_1-z_2)}{r_{12}} + \frac{(z_3-z_1)}{r_{12}} + \frac{(z_2-z_3)}{r_{23}}]e^{-\alpha(r_{12}+r_{23}+r_{31})} \\
&+ (z_1-z_2)(\nabla_1^2+\nabla_2^2+\nabla_3^2)e^{-\alpha(r_{12}+r_{23}+r_{31})})\chi_s \\
&+ \frac{2}{\sqrt{3}}(3\alpha[-\frac{(z_3-z_1)}{r_{31}} + \frac{(z_2-z_3)}{r_{23}}]e^{\alpha(r_{12}+r_{23}+r_{31})} \\
&+ [z_3-\frac{1}{2}(z_1+z_2)](\nabla_1^2+\nabla_2^2+\nabla_3^2)e^{-\alpha(r_{12}+r_{23}+r_{31})})\chi_a\}
\end{aligned} \tag{6.12}$$

The expectation value of the kinetic energy follows from integrating (6.8) time (6.12) over the three-particle positions. The orthogonality of the spin functions, splits the kinetic energy into two parts each integrating to one half of the total.

$$\langle K.E.\rangle = \frac{\hbar^2\alpha^2}{M}\frac{77}{18} \tag{6.13}$$

or in terms of (5.15)

$$\frac{\langle K.E.\rangle}{V_o} = \frac{77}{288}\frac{x^2}{K} \tag{6.14}$$

### 3. Spin-$\frac{1}{2}$ potential energy

As in the previous chapter, the potential energy is taken to be due to pair potentials. As in Eq. (5.2),

$$\begin{aligned} V(\underset{\sim}{r}_1,\underset{\sim}{r}_2,\underset{\sim}{r}_3) &= V(|\underset{\sim}{r}_3-\underset{\sim}{r}_1|,|\underset{\sim}{r}_2-\underset{\sim}{r}_3|,|\underset{\sim}{r}_1-\underset{\sim}{r}_2|) \\ &= V(r,s,t) \qquad (6.15) \\ &= V(r) + V(s) + V(t) \end{aligned}$$

$$\begin{aligned} \langle V(r_{12},r_{23},r_{31})\rangle &= 3\langle V(r_{12})\rangle \qquad (6.16) \\ &= 3(\phi_a,V(r_{12})\phi_a)+3(\phi_s,V(r_{12})\phi_s) \end{aligned}$$

Calling the interparticle distances r,s,t,

$$\langle V(r,s,t)\rangle = (2\alpha)^8 \frac{4}{9} \{ \int_0^\infty \int_0^\infty \int_{|r-s|}^{r+s} r^3 st \; V(r) e^{-2\alpha(r+s+t)} drdsdt$$

$$+ 2 \int_0^\infty \int_0^\infty \int_{|r-s|}^{r+s} rs^3 t \; V(r) e^{-2\alpha(r+s+t)} drdsdt\} \qquad (6.17)$$

4. Models

a) Spin-$\frac{1}{2}$ square well potential

We consider the pair-potential

$$V(r_{ij}) = \begin{cases} -V_o, & r_{ij} < r_o \\ 0, & \text{otherwise} \end{cases} \qquad (6.18)$$

(6.18) in (6.17) gives

$$\langle V(r,s,t)\rangle = -V_o (2\alpha)^8 \frac{4}{9} \{ \int_0^{r_o} \int_0^\infty \int_{|r-s|}^{r+s} r^3 st \; e^{-2\alpha(r+s+t)} drdsdt \qquad (6.19)$$

$$+ 2 \int_0^{r_o} \int_0^\infty \int_{|r-s|}^{r+s} rs^3 t \; e^{-2\alpha(r+s+t)} drdsdt\}$$

To the result[3] of integrations (6.19), expressed in terms of $x=4\alpha r_o$ from (5.15), add (6.14).

$$\frac{E}{V_o} = \frac{77}{288} \frac{x^2}{K} - 3 - [\frac{x^6}{1080} + \frac{x^5}{80} + \frac{13x^4}{144} + \frac{4x^3}{9} + \frac{3}{2}x^2 + 3x + 3]e^{-x}\} \qquad (6.20)$$

Numerical analysis of (6.20) gives the threshold value of K. Because this is a variational calculation the energy calculated is an upper bound to the exact energy, so that $K_c$ calculated here is an upper bound. Our result is that

$$K_c^{\mu b} = 4.077222 \; . \tag{6.21}$$

Interpretation of this and later numbers are left for the concluding chapter.

b) Spin-$\frac{1}{2}$ exponential potential

The potential

$$V(r_{ij}) = -V_o e^{-r_{ij}/r_o} \tag{6.22}$$

into (6.17) gives

$$\langle V(r,s,t)\rangle = -V_o(2\alpha)^8 \frac{4}{9} \{ \int_0^\infty \int_0^\infty \int_{|r-s|}^{r+s} r^3 st \, e^{-\frac{r}{r_o}-2\alpha(r+s+t)} drdsdt$$

$$+ 2 \int_0^\infty \int_0^\infty \int_{|r-s|}^{r+s} rs^3 t \, e^{-\frac{r}{r_o}-2\alpha(r+s+t)} drdsdt\} \tag{6.23}$$

The result of integrations (6.23) expressed in terms of $x=4\alpha r_o$ with (6.14) added on is:

$$\frac{E}{V_o} = \frac{77}{288}\frac{x^2}{K} - [\frac{2}{3}\frac{x^7}{(1+x)^7} + \frac{5}{6}\frac{x^6}{(1+x)^6} + \frac{2}{3}\frac{x^5}{(1+x)^5} + \frac{1}{2}\frac{x^4}{(1+x)^4}$$

$$+ \frac{1}{3}\frac{x^3}{(1+x)^3}] \tag{6.24}$$

Numerical analysis of (6.24) gives $K_c^{ub}$ for this potential.

$$K_c^{ub} = 2.373106 \tag{6.25}$$

c) Spin-$\frac{1}{2}$ Yukawa potential

The potential

$$V(r_{ij}) = -V_o \frac{r_o}{r_{ij}} e^{-\frac{r_{ij}}{r_o}} \tag{6.26}$$

gives

$$\begin{aligned} \langle V(r,s,t)\rangle = -V_o(2\alpha)^8 \frac{4}{9} r_o \Big\{ & \int_0^\infty\int_0^\infty\int_{|r-s|}^{|r+s|} r^2 st\, e^{-\frac{r}{r_o}-2\alpha(r+s+t)} \\ & \times drdsdt \qquad (6.27) \\ & + 2\int_0^\infty\int_0^\infty\int_{|r-s|}^{r+s} s^3 t\, e^{-\frac{r}{r_o}-2\alpha(r+s+t)} drdsdt\Big\} \end{aligned}$$

The result of (6.27) expressed in terms of $x=4\alpha r_o$ with (6.14) added on is:

$$\frac{E}{V_o} = \frac{77}{288}\frac{x^2}{K} - \left[\frac{1}{9}\frac{x^7}{(1+x)^6} + \frac{1}{6}\frac{x^6}{(1+x)^5} + \frac{1}{6}\frac{x^5}{(1+x)^4} + \frac{1}{6}\frac{x^4}{(1+x)^3} + \frac{1}{6}\frac{x^3}{(1+x)^2}\right] \tag{6.28}$$

Numerical analysis of (6.28) gives $K_c^{ub}$ for this potential.

$$K_c^{ub} = 2.834612 \tag{6.29}$$

d) Spin-$\frac{1}{2}$ Gaussian potential

The potential

$$V(r_{ij}) = V_o \, e^{-r_{ij}^2/r_o^2} \tag{6.30}$$

into (6.17) gives

$$\langle V(r,s,t)\rangle = -V_o(2\alpha)^8 \, \frac{4}{9}\Big\{ \int_0^\infty \int_0^\infty \int_{|r-s|}^{r+s} r^3 st \, e^{-\frac{r^2}{r_o^2}-2\alpha(r+s+t)} \, drdsdt$$

$$+ 2\int_0^\infty \int_0^\infty \int_{|r-s|}^{r+s} rs^3t \, e^{-\frac{r^2}{r_o^2}-2\alpha(r+s+t)} \, drdsdt\Big\} \tag{6.31}$$

The result of (6.31) expressed in terms of $\gamma=2\alpha r_o=\frac{x}{2}$ from (5.32), with (6.14) added on is:

$$\frac{E}{V_o} = \frac{77}{72}\,\frac{\gamma^2}{K} - \Big\{-\frac{8}{135}\gamma^{12} - \frac{26}{135}\gamma^{10} + \frac{1}{15}\gamma^8$$

$$+ \Big[\frac{8}{135}\gamma^{13} + \frac{2}{9}\gamma^{11} - \frac{1}{18}\gamma^7 + \frac{1}{3}\gamma^3\Big]\sqrt{\pi}e^{\gamma^2}[1-\mathrm{erf}(\gamma)]\Big\} \tag{6.32}$$

Numerical analysis of (6.32) gives

$$K_c^{ub} = 4.368196 \tag{6.33}$$

## C. Spin-$\frac{3}{2}$ Trimer

### 1. Spin-$\frac{3}{2}$ trial wavefunction

The wavefunction for the spin-$\frac{3}{2}$ trimer has the form from (4.17)

$$\phi = g_o^1 \, D_{mo}^1(\alpha,\beta,\gamma) \qquad (6.34)$$

$g_o^1$ is a function of the internal coordinates and is antisymmetric under particle exchanges. We use the antisymmetrizer (6.4) on the factor

$$(x_1-x_2)[(y_3-y_1)-(y_2-y_3)] \qquad (6.35)$$

and get

$$(x_1y_3-x_3y_1+x_2y_1-x_1y_2+x_3y_2-x_2y_3) \qquad (6.36)$$

from which we construct the trial wavefunction

$$\phi = N(x_1y_3-x_3y_1+x_2y_1-x_1y_2+x_3y_2-x_2y_3)e^{-\alpha(r_{12}+r_{23}+r_{31})} \qquad (6.37)$$

Transforming (6.37) to body-fixed coordinates using (6.1) we see that

$$\phi = 3N[\xi_2\eta_1-\xi_1\eta_2] \; D_{oo}^1(\alpha,\beta,\gamma) \qquad (6.38)$$

in agreement with (6.34) and the arguments of Section C.3 of Chapter 4.

For the volume integral (5.4) the normalization A is

$$N = \frac{2^7\alpha^5}{\sqrt{33}} \qquad (6.39)$$

### 2. Spin-$\frac{3}{2}$ kinetic energy

In rectangular coordinates, the kinetic energy operation (6.11) on (6.37) gives

$$-\frac{N\hbar^2}{2M}\quad -8\alpha[x_1y_3-x_3y_1+x_2y_1-x_1y_2+x_3y_2-x_2y_3][\frac{1}{r_{12}}+\frac{1}{r_{23}}+\frac{1}{r_{31}}]$$

$$+\ \alpha^2[x_1y_3-x_3y_1+x_2y_1-x_1y_2+x_3y_2-x_2y_3][(\hat{r}_{12}-\hat{r}_{31})^2 \qquad (6.40)$$

$$+\ (\hat{r}_{23}-\hat{r}_{12})^2\ +\ (\hat{r}_{31}-\hat{r}_{23})^2]\}\ e^{-\alpha(r_{12}+r_{23}+r_{31})}$$

Calculating the expectation value of the kinetic energy from (6.40) by multiplying by (6.37) and integrating, we get

$$<\mathrm{K.E.}> \ = \frac{48}{11}\,\frac{\hbar^2\alpha^2}{M} \ = \frac{3}{11}\,\frac{x^2}{K}\,V_o \qquad (6.41)$$

### 3. Spin-$\frac{3}{2}$ potential energy

$$<V(r_{12},r_{23},r_{31})> \ = \int_0^\infty\int_0^\infty\int_{|r-s|}^{r+s} \phi^2\ V(r,s,t)rstdrdsdt$$

by (6.15) and (6.37)

$$= [\frac{2^{12}\alpha^{10}}{33}]\int_0^\infty\int_0^\infty\int_{|r-s|}^{r+s} (-r^{s}st-2rs^5t+4r^3s^3t \qquad (6.42)$$

$$+\ 2rs^3t^3)V(r)e^{-2\alpha(r+s+t)}drdsdt$$

Doing the s and t integrals in (6.42)

$$<V(r,s,t)> = [\frac{2^{12}\alpha^{10}}{33}] \int_0^\infty V(r)e^{-4\alpha r}(\frac{r^7}{15\alpha^2}+\frac{r^6}{5\alpha^3}+\frac{r^5}{4\alpha^4}+\frac{r^4}{8\alpha^5})dr \tag{6.43}$$

4. Models

a) Spin-$\frac{3}{2}$ square well potential

In (6.43), the potential (6.18) gives

$$<V(r,s,t)> = -V_o[\frac{2^{12}\alpha^{10}}{33}] \int_0^{r_o} e^{-4\alpha r}(\frac{r^7}{15\alpha^2}+\frac{r^6}{5\alpha^3}+\frac{r^5}{4\alpha^4}+\frac{r^4}{8\alpha^5})dr \tag{6.44}$$

These integrals are done using the result

$$\int_0^{r_o} r^\eta e^{-4\alpha r}dr = -\frac{r_o^\eta e^{-4\alpha r_o}}{4\alpha} + \frac{\eta}{(4\alpha)} \int_0^{r_o} r^{\eta-1}e^{-4\alpha r}dr \tag{6.45}$$

Adding in (6.41) we get

$$\frac{E}{V_o} = \frac{3}{11}\frac{x^2}{K} -\{3-[\frac{x^7}{7920}+\frac{19x^6}{7920}+\frac{29x^5}{1320}+\frac{x^4}{8}+\frac{x^3}{2}+\frac{3x^2}{2}+3x+3]e^{-x}\} \tag{6.46}$$

Numerical analysis of (6.46) gives $K_c^{ub}$ for this potential.

$$K_c^{ub} = 7.238101 \tag{6.47}$$

### b) Spin-$\frac{3}{2}$ exponential potential

In (6.43), the potential (6.22) gives

$$<V(r,s,t)>=-V_o[\frac{2^{12}\alpha^{10}}{33}]\int_0^{\infty} e^{-[\frac{1}{r_o}+4\alpha]r}(\frac{r^7}{15\alpha^2}+\frac{r^6}{5\alpha^3}+\frac{r^5}{4\alpha^4}+\frac{r^4}{8\alpha^5})dr \tag{6.48}$$

Doing the integrals and adding in the kinetic energy from (6.41)

$$\frac{E}{V_o} = \frac{3x^2}{11K} -[\frac{7x^8}{11(1+x)^8}+\frac{12}{11}\frac{x^7}{(1+x)^7}+\frac{10}{11}\frac{x^6}{(1+x)^6}+\frac{4}{11}\frac{x^5}{(1+x)^5}] \tag{6.49}$$

Numerical analysis of (6.49) gives

$$K_c^{ub} = 5.021898 \tag{6.50}$$

### c) Spin-$\frac{3}{2}$ Yukawa potential

In (6.43), the potential (6.26) gives

$$<V(r,s,t)> =-V_o[\frac{2^{12}\alpha^{10}}{33}]r_o\int_0^{\infty} e^{-[\frac{1}{r_o}+4\alpha]r}(\frac{r^6}{15\alpha^2}+\frac{r^5}{5\alpha^3}+\frac{r^4}{4\alpha^4}+\frac{r^3}{8\alpha^5})dr \tag{6.51}$$

Doing the integrals and adding in the kinetic energy from (6.41)

$$\frac{E}{V_o} = \frac{3}{11}\frac{x^2}{K} -[\frac{1}{11}\frac{x^8}{(1+x)^7}+\frac{2}{11}\frac{x^7}{(1+x)^6}+\frac{2}{11}\frac{x^6}{(1+x)^5}+\frac{1}{11}\frac{x^5}{(1+x)^4}] \tag{6.52}$$

Numerical analysis of (6.52) gives

$$K_c^{ub} = 6.655844 \qquad (6.53)$$

d) Spin-$\frac{3}{2}$ Gaussian potential

In (6.43), the potential (6.30) gives

$$\langle V(r,s,t)\rangle = -V_o \frac{16}{33}\Big[\int_0^\infty e^{-\frac{r^2}{r_o^2} - 4\alpha r}\Big(\frac{(2\alpha r)^7}{15} \qquad (6.54)$$

$$+ \frac{2(2\alpha r)^6}{5} + (2\alpha r)^5 + (2\alpha r)^4\Big)d(2\alpha r)\Big]$$

Doing the integrals in (6.54) in terms of $\gamma = 2\alpha r_o = \frac{x}{2}$ from (5.30) and adding in the kinetic energy from (6.41),

$$\frac{E}{V_o} = \frac{12}{11}\frac{\gamma^2}{K} - \Big\{\frac{8}{495}\gamma^{14} + \frac{32}{495}\gamma^{12} - \frac{14}{165}\gamma^{10} + \frac{8}{55}\gamma^8$$

$$- \frac{4}{33}\gamma^6 + \Big[-\frac{8}{495}\gamma^{15} - \frac{4}{55}\gamma^{13} + \frac{2}{33}\gamma^{11} - \frac{1}{11}\gamma^9$$

$$+ \frac{2}{11}\gamma^5\Big]\sqrt{\pi}\, e^{\gamma^2}[1-\mathrm{erf}(\gamma)]\Big\} \qquad (6.55)$$

Numerical analysis of (6.55) gives

$$K_c^{ub} = 8.896328 \qquad (6.56)$$

# FOOTNOTES

1. R. N. Hill, J. Math. Phys. 15, 9 (1974); M. E. Rose, Elementary Theory of Angular Momentum, (Wiley, N.Y., 1957).
2. See Appendix A.
3. Three particle integrals are given in Appendix B.

# CHAPTER 7

# CONCLUSIONS

The trial wavefunctions used in the previous chapter were constructed to incorporate the exchange symmetry and the angular momenta. The numerical results of the variational calculations with these wavefunctions are summarized in Table 7-1, the four rows corresponding to the four potential models treated.

From Table 7-1, we calculate Table 7-2, a set of derived ratios that is useful in evaluating the methods used.

## A. Theorems Satisfied

### 1. Hall Post lower bound

The Hall-Post lower bound[1] on the three boson ground state energy gives a lower bound of two-thirds to column G of Table 7-2.

$$G = \frac{C}{A} \geq \frac{2}{3} \tag{7.1}$$

This is satisfied for the models considered.

Table 7-1

| BINDING PARAMETERS | 2 Body | | 3 Body | | |
|---|---|---|---|---|---|
| | A. $K_c(\ell=0)$ | B. $K_c(\ell=1)$ | C. $K_c^{ub}(\ell=0)$ | D. $K_c^{ub}\left(\substack{\ell=1\\ s=1/2}\right)$ | E. $K_c^{ub}\left(\substack{\ell=1\\ s=3/2}\right)$ |
| Square Well | $\frac{\pi^2}{4} = 2.4674$ [1] | $\pi^2 = 9.8696$ [5] | 2.096023 [9] | 4.077222 [13] | 7.238101 [17] |
| Exponential | 1.446 [2] | 7.049 [6] | 1.222041 [10] | 2.373106 [14] | 5.021898 [18] |
| Yukawa | 1.67982 [3] | 9.082 [7] | 1.462678 [11] | 2.834612 [15] | 6.655844 [19] |
| Gaussian | 2.684 [4] | 12.100 [8] | 2.247772 [12] | 4.368196 [16] | 8.896328 [20] |

[1] This follows from the exact solution to the reduced Schroedinger equation.

[2] This is from the tabulated zeros of the Bessel function in the exact treatment. Mott & Massey, *Theory of Atomic Collisions*, (1965)

[3] From Hulthen & Laurikainen, *Rev. Mod. Phys.*, *23*, 1 (1951)

[4,6,8] Numerical integration

[5] Exact solution

[7] Numerical integration; also Rogers, Gaboske, & Harwood, *Phys. Rev. A*, *1*, 1577 (1970)

[9] Equation 5.17

[10] Equation 5.22

[11] Equation 5.27

[12] Equation 5.34

[13] Equation 6.21

[14] Equation 6.25

[15] Equation 6.29

[16] Equation 6.33

[17] Equation 6.47

[18] Equation 6.50

[19] Equation 6.53

[20] Equation 6.56

Table 7-2

| REDUCED BINDING PARAMETERS | F. $\frac{B}{A}$ | G. $\frac{C}{A}$ | H. $\frac{D}{A}$ | I. $\frac{E}{A}$ | J. $\frac{D}{B}$ | K. $\frac{E}{B}$ |
|---|---|---|---|---|---|---|
| Square Well | 4.000 | .849 | 1.652 | 2.933 | .413 | .733 |
| Exponential | 4.875 | .845 | 1.641 | 3.473 | .337 | .713 |
| Yukawa | 5.407 | .871 | 1.688 | 3.962 | .312 | .733 |
| Gaussian | 4.508 | .838 | 1.628 | 3.315 | .361 | .735 |

## 2. Bruch-Sawada upper bound

There is an upper bound[2] on the three boson ground state energy. To be an improvement over this bound, our upper bound must satisfy:

$$\frac{C}{A} \leq 1 \tag{7.2}$$

This is easily true in all cases. This says that three bosons bind before two do.

## 3. Hall lower bounds for fermions

The Hall lower bound[3] for the spin-$\frac{3}{2}$ trimer relates its ground state energy to the $\ell=1$, two-body ground state energy. From it we get a lower bound to column K

$$K = \frac{E}{B} \geq \frac{2}{3} \tag{7.3}$$

(7.3) is satisfied for each case, though it is noted that our upper bounds get quite close to this lower bound.

The Hall lower bound to the spin-$\frac{1}{2}$ trimer relates its ground state energy to the first two states of the two-body problem. From this we get the lower bound to column H:

$$H = \frac{D}{A} \geq \frac{2}{3} \tag{7.4}$$

which is satisfied.

## B. Conjectures Suggested

### 1. Spin $\frac{1}{2}$ lies below spin $\frac{3}{2}$

That the spin-$\frac{1}{2}$ fermion trimer binds before the spin-$\frac{3}{2}$ trimer was suggested earlier. It seems borne out by

$$D < E \tag{7.5}$$

which is the case for each model potential.

### 2. Three fermions bind before two bind with $\ell=1$

This conjecture is based on the facts that

$$\begin{aligned} J &= \frac{D}{B} < 1 \\ K &= \frac{E}{B} < 1 \end{aligned} \tag{7.6}$$

Comparing the numbers on these columns of Table 7-2 to those for (7.2) it appears that this conjecture is very likely, though it has not been proven.

### 3. The lower bound on the spin-$\frac{1}{2}$ trimer is one half that of the spin-$\frac{3}{2}$ trimer

This is a much stronger conjecture than (7.5) and would be the analogue of (7.3). The statement is that

$$J = \frac{D}{B} \geq \frac{1}{3}$$

Looking at column J of Table 7-2, we see that this conjecture is satisfied for all but the yukawa potential. The reason why the yukawa potential is excepted can be understood in terms of the $\ell=0$ nature of its first excited state. This is suggested by the Carr Post improved lower bound.[4]

## C. Improved Upper Bounds

### 1. Boson trimers

The upper bounds calculated for the boson cases lie considerably below those previously known. Column G of Table 7-2 is bounded below by .667. The Bruch-Sawada upper bound (7.2) for this column is 1. The square well has been looked at by Sitenko and Kharchenko,[5] their value for our column G is 0.8. Humberston, Hall, and Osborn[6] have studied the exponential and yukawa potentials. Our values agree with theirs within the plotting accuracy of their graphs.

### 2. Fermion trimers

a) Spin-$\frac{3}{2}$

The Hall lower bound (7.3) in column K is .667. Our upper bound comes extremely close to this lower bound thus determining the threshold binding parameter quite well.

b) Spin-$\frac{1}{2}$

Our upper bounds in column J come extremely close to the conjectured lower bounds.

## D. Future Applications

The four potentials studied here indicate that the form of the trial functions used is essentially correct and that the method of incorporating symmetry requirements here will extend to more realistic cases.

More specific numerical results for physical trimers require that more appropriate potential models be treated instead; models that more closely describe the intermolecular forces are, for example, the Lennard-Jones 12-6 potential or the Morse potential. The qualitative difference of the more realistic molecular models from those treated here is in the relatively thick cores of the potentials.

While most of the algebraic simplicity of the variational energy expressions will be lost in going to more complicated potentials, and while numerical solutions seem almost certain, nevertheless, it is hoped that the bounds derived on the binding parameters for the more realistic potentials will be equally as good as those for the four models studied here.

It is also believed that the same approach is also applicable to other few body problems such as the four-body problem, though little information exists about these.

# FOOTNOTES

1. R. L. Hall and H. R. Post, Proc. Phys. Soc. London 90, 381 (1967).
2. L. W. Bruch and K. Sawada, Phys. Rev. Letters 30, 25 (1973).
3. R. L. Hall, J. Phys. A, 1, 468 (1968).
4. R. J. M. Carr and H. R. Post, Phys. A, 4, 665 (1971).
5. A. G. Sitenko, V. F. Kharchenko, Sov. Phys. Uspekhi, 14, 125 (1971), p. 141, Fig. 6.
6. J. W. Humberston, R. L. Hall, and T. A. Osborne, Phys. Letters 27B, 195 (1968).

# APPENDIX A

## RIGID ROTOR WAVEFUNCTIONS FOR $\ell=1$

$$D^1_{00} = \cos\beta$$

$$D^1_{01} = e^{i\gamma}\frac{1}{\sqrt{2}}\sin\beta = \frac{1}{\sqrt{2}}(\cos\gamma + i\sin\gamma)\sin\beta$$

$$D^1_{0\,-1} = -e^{-i\gamma}\frac{1}{\sqrt{2}}\sin\beta = \frac{1}{\sqrt{2}}(-\cos\gamma + i\sin\gamma)\sin\beta$$

$$D^1_{10} = -e^{i\alpha}\frac{1}{\sqrt{2}}\sin\beta$$

$$D^1_{11} = e^{i(\alpha+\gamma)}\frac{1}{2}(1 + \cos\beta) = e^{i(\alpha+\gamma)}\cos^2\frac{\beta}{2}$$

$$D^1_{1\,-1} = e^{i(\alpha-\gamma)}\frac{1}{2}(1 - \cos\beta) = e^{i(\alpha-\gamma)}\sin^2\frac{\beta}{2}$$

$$D^1_{-1\,0} = e^{-i\alpha}\frac{1}{\sqrt{2}}\sin\beta$$

$$D^1_{-1\,1} = e^{-i(\alpha-\gamma)}\frac{1}{2}(1 - \cos\beta) = e^{-i(\alpha-\gamma)}\sin^2\frac{\beta}{2}$$

$$D^1_{-1\,-1} = e^{-i(\alpha+\gamma)}\frac{1}{2}(1 + \cos\beta) = e^{-i(\alpha+\gamma)}\cos^2\frac{\beta}{2}$$

# APPENDIX B

## THREE-PARTICLE VOLUME INTEGRALS

$$I(\ell,m,n) \equiv \int_{r=0}^{\infty} \int_{s=0}^{\infty} \int_{t=|r-s|}^{r+s} r^{\ell} s^{m} t^{n} e^{-a(r+s+t)} \, dr \, ds \, dt$$

| $\ell$ | $m$ | $n$ | $I(\ell,m,n)$ |
|---|---|---|---|
| -1 | 1 | 1 | $(5/12)a^{-4}$ |
| 1 | 1 | 0 | $(5/16)a^{-5}$ |
| 1 | 1 | 1 | $(7/16)a^{-6}$ |
| 2 | 1 | 0 | $(9/16)a^{-6}$ |
| 2 | 1 | 1 | $(7/8)a^{-7}$ |
| 2 | 2 | 1 | $(31/16)a^{-8}$ |
| 3 | 0 | 0 | $(3/4)a^{-6}$ |
| 3 | 1 | 0 | $(21/16)a^{-7}$ |
| 3 | 1 | 1 | $(9/4)a^{-8}$ |
| 3 | 2 | 0 | $(51/16)a^{-8}$ |
| 3 | 2 | 1 | $(351/64)a^{-9}$ |
| 3 | 2 | 2 | $(435/32)a^{-10}$ |
| 3 | 3 | 0 | $(621/64)a^{-9}$ |
| 3 | 3 | 1 | $(1089/64)a^{-10}$ |
| 4 | 1 | 0 | $(15/4)a^{-8}$ |
| 4 | 1 | 1 | $(225/32)a^{-9}$ |
| 4 | 2 | 1 | $(75/4)a^{-10}$ |
| 4 | 3 | 0 | $(1125/32)a^{-10}$ |
| 5 | 0 | 0 | $(45/8)a^{-8}$ |
| 5 | 1 | 0 | $(405/32)a^{-9}$ |
| 5 | 1 | 1 | $(825/32)a^{-10}$ |
| 5 | 2 | 0 | $(1245/32)a^{-10}$ |
| 6 | 1 | 0 | $(1575/32)a^{-10}$ |
| 7 | 0 | 0 | $(315/4)a^{-10}$ |