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Hamiltonian Matrix Elements from a Symmetric Wave Function*

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The matrix elements of a c.m. transformed molecular Hamiltonian for a wave function constructed from a symmetrized product of one-particle orthonormal spin functions are given in terms of the integrals over the coordinates of the particles. These matrix elements are necessary to study the structure of deuterated molecules such as D_2O, ND_3, CD_4, etc. The integrals are the same as those found for antisymmetric wave functions with the exception of the two-particle integrals of the form $\int g_i^*(1) g_i^*(2)\ (r_{12})^{-1} g_j(1) g_j(2)\, dV$, when two bosons occupy the same spin function. There are, however, significant differences in the matrix elements.

I. INTRODUCTION

We have discussed the protonic structure of molecules in several papers.[1] A natural extension of that work is the investigation of the structure of deuterons in molecules. Deuterons, however, give rise to different matrix elements than those found for electrons or protons, since they are bosons.

In this paper, we give the matrix elements for symmetric wave functions made from products of single-particle functions.

II. SYMMETRIC WAVE FUNCTION

The wave functions which we will use will be a sum of products of orthonormal spin functions such as

$$g_1(n_1) g_2(n_2) \cdots g_x(n_x) .$$

The n_i's represent occupation numbers, or the number of bosons in g_i, and $\sum_i n_i = N$, where N is the total number of particles. The wave function is the sum of all permutations of the N bosons, or

$$\psi = (N!)^{-1/2}\sum_{P'}P'[g_1(n_1)g_2(n_2)\cdots g_x(n_x)]\ ,$$

but the permutations which interchange bosons within a function do not change ψ. There are $n_1!\,n_2!\cdots n_x!$ such permutations. Our normalized function is, therefore,

$$\psi = (n_1!\,n_2!\cdots n_x!\,N!)^{-1/2}\sum_{P'}P' \times[g_1(n_1)g_2(n_2)\cdots g_x(n_x)]\ .$$

III. OVERLAPS

We will consider first the overlap of G_a with itself. This integral is

$$S_{aa}=(\textstyle\prod_i n_i!\,N!)^{-1}\int\sum_{Q'}Q'[g_1(1)\cdots g_1(n_1)\cdots \times g_x(N-n_x+1)\cdots g_x(N)\sum_{P'}P'[g_1(1)\cdots \times g_1(n_1)\cdots g_x(N-n_x+1)\cdots g_x(N)]\,dV\ ,$$

but all permutations Q' and P' which exchange bosons within a function do not change either G_a or G_b; hence, these permutations do not change S_{aa}. There will be $\Pi_i n_i!$ such permutations among the Q' and $\Pi_i n_i!$ among the P', which when carried out leave

$$S_{aa}=(\textstyle\prod_i n_i!/N!)\int\sum_Q Q[g_1(1)\cdots g_x(N)]^* \times\sum_P P[g_1(1)\cdots g_x(N)]\,dV\ ,$$

where Q and P are the permutations which exchange bosons between different functions. Now we can perform the inverse of each Q which does not affect G_b, since it contains all permutations already or the integral because we are in effect just relabeling the variables of integration to get

$$S_{aa}=\int g_1^*(1)\cdots g_1^*(n_1)\cdots g_x^*(N-n_x+1)\cdots \times g_x^*(N)\sum_P P[g_1(1)\cdots g_1(n_1)\cdots g_x(N-n_x+1)\cdots \times g_x(N)]\,dV\ ,$$

since there remain $N!/\prod_i n_i!\,Q$ permutations.

Any permutation P, except for the identity permutation, will lead to overlap between orthogonal functions, which will make S_{aa} vanish. Therefore, our integral becomes

$$S_{aa}=\textstyle\prod_i[\int g_i^*(1)g_i(1)\,dV_1]^{n_i}\ ;$$

but, of course, each integral in this equation is equal to 1, thus we find $S_{aa}=1$.

A symmetric function G_a may differ from and be orthogonal to another symmetric function G_b in the following ways: (i) The functions G_a and G_b may have the same basis functions g_i but different occupation numbers; (ii) G_a and G_b may differ in basis functions but not in occupation numbers; (iii) G_a and G_b may differ in both basis functions and occupation numbers; (iv) G_a and G_b may differ in the number of basis functions that each has; (v) G_a may differ in the number and type of basis functions. We will now show that $S_{ab}=0$ for all the cases described above.

Case 1. In this case the basis functions are the same, but all or some of the n_i of G_a are unequal to the m_i of G_b. The overlap integral S_{ab} is

$$S_{ab}=(\textstyle\prod_i n_i!\prod_i m_i!)^{-1/2}(N!)^{-1}\int\sum_{Q'}Q'[g_1(1)\cdots \times g_1(n_1)\cdots g_i(N-n_i+1)\cdots g_i(N)]^* \times\sum_{P'}P'[g_1(1)\cdots g_1(m_1)\cdots g_i(N-m_i+1)\cdots \times g_i(N)]\,dV$$

When we carry out the Q' and P' permutations which permute bosons within a function, we get

$$S_{ab}=(\textstyle\prod_i n_i!\prod_i m_i!)^{1/2}\ (N!)^{-1} \times\int\sum_Q Q[g_1(1)\cdots g_i(N)]^* \times\sum_P P[g_1(1)\cdots g_i(N)]\,dV\ .$$

That becomes

$$S_{ab}=(\textstyle\prod_i m_i!/\prod_i n_i!)^{1/2}\int g_1^*(1)\cdots g_i^*(N) \times\sum_P P[g_1(1)\cdots g_i(N)]\,dV\ ,$$

when we perform the $N!/\prod_i n_i$ inverse Q operations. From this expression, we get our final result. We have already shown that any P' other than the identity leads to a vanishing integral even when all $n_i=m_i$. If some of the n_i are different from the m_i, then even the identity operation gives a vanishing integral. Suppose that $n_r>m_r$, which necessarily means that some $n_s<m_s$ and furthermore, that $n_r=m_s$ and $n_s=m_r$; then the integral is

$$S_{ab}=\prod_{i\neq r,s}[\int g_i^*(1)g_i(1)\,dV_1]^{n_i} \times[\int g_r^*(1)g_r(1)\,dV_1]^{n_r}[\int g_s^*(1)g_r(1)\,dV_1]^{n_r-m_r} \times[\int g_s^*(1)g_s(1)\,dV_1]^{m_s}=0\ ,$$

since the overlap between g_s and g_r is zero.

Case 2. In this case, the occupation numbers are the same, but the basis functions are different. Suppose that g_i is in G_a occupied by n_i bosons, and g'_i is in G_b occupied by n_i bosons. One can easily see that S_{ab} is 0 by looking at the development of S_{aa} and noting that regardless of the permutation P' there will always be overlaps either between a g_i and a g'_i and/or between a g_i and a g_j. For the same reason, the integral vanishes when G_a and G_b differ by more than one basis function.

Case 3. This case leads to $S_{ab}=0$ for the same reasons that were given for case 1 or case 2.

Case 4. Suppose that G_a has x basis functions and G_b has y basis functions, and that $x=y+1$, and all g_i for $i=1$ to y are the same for both G_a and G_b. Then we find that at least one $n_i < m_i$. We can relabel the variables of integration such that it is $n_y < m_y$. It is also true that $n_y + n_x = m_y$. We know that all permutations P' which exchange bosons among the g_i of G_b will lead to a vanishing integral except for the identity, and that leads to

$$S_{ab} = (m_y!/n_x!\,n_y!)^{1/2} \prod_{i\neq y} [\int g_i^*(1) g_i(1)\,dV_1]^{n_i} \times [\int g_y^*(1) g_y(1)\,dV_1]^{n_y} [\int g_x^*(1) g_y(1)\,dV_1]^{n_x} ;$$

but the overlap between g_x and g_y is 0; therefore, we have $S_{ab}=0$.

Case 5. In this case, G_a and G_b differ in the number and in the type of basis functions. Here, $S_{ab}=0$ for one or all of the reasons previously given.

IV. MATRIX ELEMENTS OF HAMILTONIAN

The integral involving the Hamiltonian are more complicated but just as straightforward as the overlap integral. We will begin with the one-deuteron integrals. These are

$$U_{ab} = \int G_a^* \sum_A u_A G_b\,dV ,$$

where,

$$u_A = -(1/2\mu_d)\nabla_A^2 + (Z/r_A) ,$$

and where

$$\mu_d = (m m_d/m + m_d) ,$$

where m_d is the mass of the deuteron, Z is the charge of the atom chosen as the origin of the relative coordinate system, and r_A is the distance from the deuteron to that atom. The simplest integral is the one with $G_a = G_b$. After we perform all the trivial Q' and P' permutations and the inverse Q permutations which do not affect $\sum_A u_A$ (since this is a symmetric operator), this integral will be

$$U_a = \int g_1^*(1)\cdots g_x^*(N) \sum_A u_A \times \sum_P P[g_1(1)\cdots g_x(N)]\,dV .$$

Any permutation P other than the identity leads to overlaps over orthogonal functions. For the identity, we find that for each A we will get one integral of the form

$$\int g_r^*(A) u_A g_r(A)\,dV_A ,$$

and since there are n_r such integrals for

$$A = 1 + \sum_{i=1}^{r-1} n_i \quad \text{through} \quad A = n_r + \sum_{i=1}^{r-1} n_i ,$$

we will, in fact, get n_r such integrals, but this is true for all n_i. Therefore, we have

$$U_a = \sum_i n_i \int g_i^*(1) u_1 g_i(1)\,dV_1 .$$

Each of the five cases which we have considered for the overlap integrals gives a different result.

Case 1. We will suppose that G_a differs from G_b because two of the n_i's are different. Say that $n_r > m_r$; hence, we find that some $n_s < m_s$ such that $n_r = m_s$ and $n_s = m_r$. In this case, only the permutations P which place the deuterons of G_b into coincidence with those of G_a for all g_i $i \neq r$ or s will lead to nonvanishing integrals. Furthermore, any u_A other than an A labeling a deuteron in g_r or g_s will lead to a vanishing integral, because for any of those u_A's there will always be at least one overlap between a g_r and a g_s. Our integral is, therefore,

$$U_{ab} = \prod_{i\neq r,s} [\int g_i^*(1) g_i(1)\,dV_1]^{n_i} \times \int g_r^*(1)\cdots g_r^*(n_r) g_s^*(n_r+1)\cdots g_s^*(N) \sum_A u_A \times \sum_P P[g_r(1)\cdots g_r(m_r) g_s(m_r+1)\cdots g_s(N)]\,dV ,$$

where the permutations P are only those which affect the $n_r + n_s$ deuterons. A runs from 1 to $N = n_r + n_s = m_r + m_s$, and $dV = dV_1 \cdots dV_{n_s+n_r}$. The overlaps, of course, equal unity. Consider the case $n_r = m_r + 1$. Any P which affects the last $m_s - 1$ deuterons will lead to a vanishing integral, because for these permutations we will have more than one integral involving the orthogonal orbitals g_r and g_s, at lease one of which will be an overlap for any A. For example, consider the permutation leading to

$$U_{ab}(P) = \int g_r^*(1)\cdots g_r^*(n_r) g_s^*(n_r+1)\cdots g_s^*(N) \times \sum_A u_A g_s(1)\cdots g_r(m_r) g_s(m_r+1)\cdots g_r(N)\,dV .$$

For $A=1$, we get

$$U_{ab}(P) = \int g_r^*(1) u_1 g_s(1)\,dV_1 \int g_r^*(n_r) g_s(m_r+1)\,dV_{n_r} \times \int g_s^*(N) g_r(N)\,dV_N = 0 .$$

The result is the same for any A, and any other P of this type will give a similar result. Therefore, we only need to consider the m_r permutations which exchange the m_r+1 deuteron in g_s with the m_r deuterons in g_r plus the identity. Each one of these n_r permutations will give one nonvanishing integral. Let us see how this happens:

$$U_{ab}(A) = \int g_r^*(1)\cdots g_r^*(A)\cdots g_r^*(n_r) g_s^* \times (n_r+1)\cdots g_s^*(N) u_A \sum_P P[g_r(1)\cdots g_r(m_r) \times g_s(m_r+1)\cdots g_s(N)]\,dV ,$$

where $A \leq n_r$.

There is one P which places A in g_s and m_r+1 in g_r such that

$$U_{ab}(A) = [\int g_r^*(1) g_r(1)\,dV_1]^{n_r-1} \times [\int g_s(1) g_s(1)\,dV_1]^{n_s} \int g_r^*(A) u_A g_s(A)\,dV_A = \int g_r^*(1) u_1 g_s(1)\,dV_1 ,$$

but we will get a similar result for each $A \leq n_r$.

For $A > m_r$, we will get for any P at least one overlap between g_r and g_s. Therefore, we have

$$U_{ab}=n_r\int g_r^*(1)u_1 g_s(1)\,dV_1\ .$$

If $n_r > m_r+1$, then $U_{ab}=0$ because, regardless of the permutation P or the U_A, there will always be at least one overlap integral between a g_r and a g_s orbital. Now, if more than two of the n_i are different from the m_i, $U_{ab}=0$, because for any A there is no way to avoid overlap integrals over orthogonal orbitals. Therefore,

$$U_{ab}=n_r\int g_r^*(1)u_1 g_s(1)\,dV_1\,\delta(n_r, m_r+1)\times\delta(n_s, m_s-1)\prod_{i\neq r,s}\delta(n_i, m_i).$$

Case 2. Suppose that g_r is in G_a and orthogonal to g_r' which is in G_b and that $n_i=m_i$ for all i. The result for this case is

$$U_{ab}=n_r\int g_r^*(1)u_1 g_r'(1)\,dV_1\,\delta(n_r, m_r)\times\prod_{i\neq r,s}\delta(n_i, m_i),$$

since only the identity permutation gives a contribution. If G_a differs from G_b by more than one function, then $U_{ab}=0$.

Case 3. This case is the same as case 2 but not all of the $n_i=m_i$. Here we have $U_{ab}=0$.

Case 4. In this case, G_a has y basis functions and G_b has x basis functions. Suppose that $y=x+1$, $n_i=m_i$ for all $i=1, x-1$, and $n_r+n_y=m_x$. Then, if we have arranged the g_i such that we have $r=y-1=x$, we find that any permutation involving the deuterons labeled 1 through $\sum_{i=1}^{y-2}n_i$ will give zero contribution. Therefore we have

$$U_{ab}=(m_x!/n_x!\,n_y!)^{1/2}\int g_x^*(1)\cdots g_x^*(n_x)g_y^*\times(n_x+1)\cdots g_y^*(N)\textstyle\sum_A u_A g_x(1)\cdots g_x(m_x)\,dV\ .$$

For $A=1$ through $A=n_x$, we get zero contribution because of overlaps between g_y and g_x. If $n_y>1$, we find that $U_{ab}=0$; but for $n_y=1$, we get

$$U_{ab}=m_x^{1/2}\int g_y^*(1)u_1 g_x(1)\,dV_1\,\delta(n_x, m_x-1)\times\prod_{i\neq x \text{ or } y}\delta(n_i, m_i)\ .$$

Case 5. For this case, we have $U_{ab}=0$.

We will now consider the development of the integrals involving the two-particle operator

$$w_{AB}=(1/r_{AB})-(1/m)\nabla_A\cdot\nabla_B\ .$$

We will begin again with the $G_a=G_b$ case. The integral is

$$W_a=\int G_a^*\sum_A\sum_{B>A}w_{AB}G_a\,dV_A\,dV_B$$
$$=\int g_1^*(1)\cdots g_x^*(N)\sum_A\sum_{B>A}w_{AB}\times\sum_P P[g_1(1)\cdots g_x(N)]\,dV_A\,dV_B\ .$$

Now A and B can be in one g_i or A can be in g_i and B can be in g_j. For the first possibility, we find that only the identity permutation gives a nonvanishing contribution. This contribution is

$$\textstyle\sum_i[\frac{1}{2}n_i(n_i-1)]I_i\ ,$$

where

$$I_i=\int g_i^*(1)g_i^*(2)w_{12}g_i(1)g_i(2)\,dV_1\,dV_2\ .$$

Note that this integral cannot occur for fermions.

For the second possibility, we find that for each A and B there are two permutations which give nonvanishing contributions. These are the identity and the one which exchanges A and B. This contribution is

$$\sum_{ini}\sum_{j>i}n_j[J_{ij}+K_{ij}]\ ,$$

where

$$J_{ij}=\int g_i^*(1)g_j^*(2)w_{12}g_i(1)g_j(2)\,dV_1\,dV_2\ ,$$

$$K_{ij}=\int g_i^*(1)g_j^*(2)w_{12}g_i(2)g_j(1)\,dV_1\,dV_2\ ;$$

thus, we have

$$W_a=\sum_i[\tfrac{1}{2}n_i(n_i-1)]I_i+n_i\sum_{j>i}n_j(J_{ij}+K_{ij})\ .$$

We will now proceed with cases 1 – 5 as before.

Case 1. Suppose that $n_i=m_i$ for all i except r and s and that $n_r>m_r$, which implies that $n_s<m_s$, $n_r=m_s$, and $n_s=m_r$. We will arrange the variables of integration so that g_r and g_s are the last two orbitals. Our integral is

$$W_{ab}=\int g_1^*(1)\cdots g_1^*(n_1)\cdots g_r^*(N_r+n_r)\cdots g_r^*\times(N_r+n_r)g_s^*(N_r+n_r+1)\cdots g_s^*(N)\times\sum_A\sum_{BA}w_{AB}\sum_P P\,[g_1(1)\ldots g_1(m_1)\times\cdots g_r(M_r+1)\cdots g_r(M_r+m_r)\times g_s(M_r+n_r+1)\cdots g_s(N)\,]\,dV\ ,$$

where

$$N_r=\sum_{i=i}^{r-1}n_i\ \text{and}\ M_r=\sum_{i=i}^{r-1}m_i\ .$$

Any permutation which exchanges a deuteron in g_r or g_s with one in any g_i, $i\neq r, s$ gives zero contribution to W_{ab}, because regardless of w_{AB} there will always be an overlap between orthogonal orbitals. Furthermore, any integral involving w_{AB} for A and B not in g_r or g_s will give zero contribution for the same reason. Therefore, we have

$$W_{ab}=\int g_r^*(1)\cdots g_r^*(m_r)g_s^*(m_r+1)\cdots g_s^*(N)\times\sum_A\sum_{B>A}w_{AB}\sum_P P[g_r(1)\cdots g_r(m_r)$$

$$\times g_s(m_r+1)\cdots g_s(N)\,]\,dV\ ,$$

where now $N=n_r+n_s=m_r+m_s$, A and B range from 1 to N, and the permutations P involve only the n_r+n_s deuterons. Now suppose that $n_r=m_r+2$ and $n_s=m_s-2$. If A and B are both in g_r on the left-hand side of the operator, only the permutation which exchanges A and B with m_r+1 and m_r+2 will give a contribution to W_{ab}. But this is true for all A and $B\le n_r$. Therefore, we have

$$W_{ab}=\tfrac{1}{2}n_r(n_r-1)\int g_r^*(1)g_r^*(2)w_{12}g_s(1)\times g_s(2)\,dV_1dV_2\,\delta(n_r,\,m_r+2)\,\delta(n_s,\,m_s-2)\times\prod_{i\ne r,s}\delta(n_i,\,m_i)\ ,$$

since for all A and $B>n_r$ we get zero contribution and similarly for $A\le n_r$ and $B>n_r$.

If we have $n_r=m_r+1$ and $n_s=m_r-1$, we find again that A and $B\le m_r$ for the nonzero contributions; but we now have two permutations for each A and B that give nonzero contributions. These are the identity and the permutation which exchanges A and B. Since this is true for all A and $B\le n_r$, we get

$$W_{ab}=\tfrac{1}{2}n_r(n_r-1)\int g_r^*(1)g_r^*(2)w_{12}g_r(1)\times g_s(2)\,dV_1dV_2+\int g_r^*(1)g_r^*(2)\times w_{12}g_r(2)g_s(1)\,dV_1dV_2\ \delta(n_r,\,m_r+1)\times\delta(n_s,\,m_s-1)\prod_{i\ne r,s}\delta(n_i,\,m_i)\ .$$

If $n_r=m_r+1$, $n_s=m_s-1$, $n_t=m_t+1$, and $n_u=m_u-1$, our integral becomes

$$W_{ab}=\int g_r^*(1)\cdots g_r^*(n_r)g_s^*(n_r+1)\cdots g_s^*(n_r+n_s)\times g_t^*(n_r+n_s+1)\cdots g_r^*(n_r+n_s+n_s)\cdots g_u^*(n_r+n_s+n_t+1)\cdots g_r^*(N)\sum_A\sum_{B>A}w_{AB}\times\sum_P P[g_r(1)\cdots g_t(N)\,]\,dV\ .$$

We find that we get nonzero contributions only when A is in g_r and B is in g_t on the left of the operator. For these A and B, two permutations, the identity and the one which exchanges A and B, give nonzero contributions. The result is that

$$W_{ab}=n_rn_t\int g_r^*(1)g_t^*(2)w_{12}g_s(1)g_u(2)\,dV_1dV_2+\int g_r^*(1)g_t^*(2)w_{12}g_s(2)g_u(1)\,dV_1dV_2\times\delta(n_r,\,m_r+1)\,\delta(n_s,\,n_s-1)\,\delta(n_t,\,m_t+1)\times\delta(n_u,\,m_u-1)\prod_{i\ne r,s,t,u}\delta(n_i,\,m_i).$$

If the n_i differ from the m_i in any other way, then $W_{ab}=0$.

Case 2. Suppose that G_a differs from G_b by one basis function. That is, G_a has g_r where G_b has g_r'; all $n_i=m_i$. If $n_r>2$, the integral vanishes because there is no way to avoid an overlap integral over orthogonal functions. If $n_r=2$, then only w_{AB} with A and B in g_r of G_a will make a contribution; but this means that only the identity permutation can make a contribution. Therefore, we have

$$W_{ab}=\int g_r^*(1)g_r^*(2)w_{12}g_r'(1)g_r'(2)\,dV_1dV_2\times\delta(n_r,\,2)\prod_i\delta(n_i,\,m_i)\ .$$

If G_a differs from G_b by two functions, e.g., $g_r\ne g_r'$ and $g_s\ne g_s'$, where g_r and g_s are in G_a and g_r' and g_s' are in G_b, then we have $n_r=m_r=1$ and $n_s=m_s=1$ for the integral not to vanish, and only w_{AB} with A in g_r and B in g_s will make a contribution. Therefore, we have

$$W_{ab}=\Big[\int g_r^*(1)g_s^*(2)w_{12}g_r'(1)g_s'(2)\,dV_1dV_2+\int g_r^*(1)g_r^*(2)w_{12}g_r'(2)g_s'(1)\,dV_1dV_2\Big]\times\prod_i\delta(n_i,\,m_i)\ .$$

If G_a differs from G_b by three basis functions, then $W_{ab}=0$.

Case 3. In this case G_a and G_b differ by having different basis functions and different occupation numbers. The integral is 0 unless G_a and G_b differ by only one basis function. If it is the rth function that is different, two relations between the n_i and m_i lead to a nonvanishing integral. The first is $n_r=m_r+1=2$, $n_s=m_s-1$, and $n_i=m_i$ for all $i\ne r$ or s, which leads to

$$W_{ab}=(\tfrac{1}{2}m_s)^{1/2}\Big[\int g_r^*(1)g_r(2)g_r'(1)g_s(2)\,dV_1dV_2+\int g_r^*(1)g_r^*(2)w_{12}g_r'(2)g_s(1)\,dV_1dV_2\times\delta(m_r,\,2)\,\delta(m_r,\,m_r+1)\,\delta(m_s,\,m_s-1)\times\prod_{i\ne r,s}\delta(n_i,\,m_i)\ .$$

The second relation is $n_r=m_r=1$, $n_s=m_s-1$, $n_t=m_t+1$ and $n_i=m_i$ for all $i\ne r,\ s,\ t$, which leads to

$$W_{ab}=(m_sn_t)^{1/2}\Big[\int g_r^*(1)g_t^*(2)w_{12}g_r'(1)g_s(2)\times dV_1dV_2+\int g_r^*(1)g_t^*(2)w_{12}g_r'(2)g_s(1)\,dV_1dV_2\Big]\times\delta(n_r,\,1)\,\delta(n_r,\,m_r)\,\delta(n_s,\,m_s-1)\,\delta(n_t,\,m_t+1)\times\prod_{i\ne r,s,t}\delta(n_i,\,m_i)\ .$$

Case 4. In this case, G_a and G_b differ in the number of functions. Let G_a have x basis functions and G_b have y basis functions such that $x<y$. If $x=y+3$, then the integral vanishes. If $y=x+2$, then we must have some g_r in G_a with n_r deuterons, and g_r, g_s, g_t in G_b with m_r deuterons, such that $n_r=m_r+2$ and $n_s=m_t=1$, if the integral is not to vanish. The nonvanishing contributions to the integral are

$$W_{ab}=(m_r!/n_r!)^{1/2}\int g_r^*(1)\cdots g_r^*(n_r)\sum_A\sum_{B>A}w_{AB}$$
$$\times\sum_P P[g_r(1)\cdots g_r(m_r)g_s(m_r+1)g_t(n_r)]$$
$$=\tfrac{1}{2}[n_r(n_r-1)]^{1/2}[\int g_r^*(1)g_r^*(2)w_{12}g_s(1)$$
$$\times g_t(2)\,dV_1dV_2+\int g_r^*(1)g_r^*(2)w_{12}g_s(2)g_t(1)$$
$$\times dV_1dV_2]\,\delta(n_r,m_r+2)\prod_{i\neq r,s,t}\delta(n_i,m_i)\ .$$

If $x=y+1$, then we will get a nonvanishing integral if some g_r in G_a has n_r deuterons and some g_r and g_s in G_b have m_r and m_s deuterons, such that $n_r=m_r+2$ and $m_s=2$ or $n_r=m_r+1$ and $m_s=1$. For the first possibility, we get

$$W_{ab}=[\tfrac{1}{2}n_r(n_r-1)]^{1/2}\int g_r^*(1)g_r^*(2)w_{12}g_s(1)$$
$$\times g_s(2)\,dV_1dV_2\,\delta(n_r,m_r+2)\,\delta(m_s,2)$$
$$\times\prod_{i\neq r,s}\delta(n_i,m_i)\ ,$$

and for the second possibility, we get

$$W_{ab}=\tfrac{1}{2}n_r^{1/2}(n_r-1)\,[g_r^*(1)g_r^*(2)w_{12}g_r(1)g_s(2)$$
$$\times dV_1dV_2+\int g_r^*(1)g_r^*(2)w_{12}g_r(2)g_s(1)\,dV_1dV_2]$$
$$\times\delta(n_r,m_r+1)\,\delta(m_s,1)\prod_{i\neq r,s}\delta(n_i,m_i)\ .$$

Case 5. In this case G_a and G_b differ both in kind and in number of basis functions. Suppose that G_a has g_r where G_b has g_r', and G has x basis functions while G_b has y basis functions with $x<y$, then

$$W_{ab}=(m_1!\cdots m_y!/n_1!\cdots n_x!)^{1/2}\int g_1^*(1)\cdots$$
$$\times g_1^*(n_1)\cdots g_r^*(N_r+1)\cdots g_r^*(N_r+n_r)\cdots g_x^*(N)$$
$$\times\sum_A\sum_{B>A}w_{AB}\sum_P P[g_1(1)\cdots g_1(m_1)\cdots$$
$$\times g_r'(M_r+1)\cdots g_r'(M_r+m_r)\cdots g_y(N)\,dV\ .$$

We know from case 2 that $W_{ab}=0$ unless $n_r=m_r=2$ and all other $n_i=m_i$. Since we cannot satisfy the second condition, we know that n_r cannot equal 2 and be equal to m_r. However, if we look at the first relation between the n's and m's of case 3 and set $n_s=0$, we will get a nonzero contribution. That is, if $n_r=m_r+1=2$, and $m_s=1$, where g_s is the basis function in G_b, which does not appear in G_a, we will get

$$W_{ab}=2^{-1/2}[\int g_r^*(1)g_r^*(2)w_{12}g_r'(1)g_s(2)\,dV_1dV_2$$
$$+\int g_r^*(1)g_r^*(2)w_{12}g_r'(2)g_s(1)\,dV_1dV_2]\,\delta(n_r,2)$$
$$\times\delta(n_r,m_r+1)\,\delta(m_s,1)\prod_{i\neq r,s}\delta(n_i,m_i)\ .$$

The second relation, again with $n_s=0$, will lead to

$$W_{ab}=n_t^{1/2}[\int g_r^*(1)g_t^*(2)w_{12}g_r'(1)g_s(2)\,dV_1dV_2$$
$$+\int g_r^*(1)g_t^*(2)w_{12}g_r'(2)g_s(1)\,dV_1dV_2]$$
$$\times\delta(m_r,1)\,\delta(m_r,m_r)\,\delta(m_s,1)\,\delta(n_t,m_t-1)$$
$$\times\prod_{i\neq r,s,t}\delta(n_i,m_i)\ .$$

If G_a differs from G_b by two functions, and G_b has more basis functions than G_a, then $W_{ab}=0$, since we cannot have all $n_i=m_i$ as was shown to be necessary in case 2. If G_a differs from G_b by three or more functions, then $W_{ab}=0$.

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[1] I. L. Thomas, Chem. Phys. Letters 3, 705 (1969); Phys. Rev. 185, 90 (1969); and Phys. Rev. A 2, 75 (1970).