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A Hartree–Fock–Roothaan analogon using the principle of variance minimization

II. Test of the iteration procedure

Gerhard Pauli and Heinz Kleindienst

Institut für Physikalische Chemie I der Universität Düsseldorf, Universitätsstr. 1, D-4000 Düsseldorf 1, Federal Republic of Germany

The variance-minimizing Roothaan-like equation derived in a preceding paper [1] gives rise to a double iteration procedure. The procedure is tested by application on some simple atomic systems, using Slater-type basis functions. The integrals needed for atomic systems and Slater-type basis functions are solved.

Key words: Eigenvalue problems.

1. Discussion of the procedure

In a preceding paper [1] we showed that Variance Minimization [2, 3], for an ansatz of the wavefunction Ψ as a Slater determinant, leads to a Roothaan-like matrix equation

$$Q\boldsymbol{c}_i = \chi_i \cdot S\boldsymbol{c}_i \tag{1}$$

determining the coefficient vectors $\boldsymbol{c}_i$ of a variance-minimizing set of orbitals.

As the operator Q itself depends on the orbitals we have to solve the equation iteratively: starting from an initial set of orbitals—which may be, for example, the Hartree–Fock orbitals—we compute a matrix Q, solve the matrix equation (1) to obtain new orbitals (filling those with the lowest χ_i with electrons), compute a new Q matrix from these orbitals and so on—just like the corresponding Roothaan procedure.

Offprint requests to: G. Pauli

As the result of this iteration we obtain the Slater determinant minimizing F^2 with respect to a given λ^*. If we have started, for example, with a Hartree–Fock value as λ^* (and, say, the corresponding Hartree–Fock function as the start function) the function obtained by this procedure will, in general, *not* be the Hartree–Fock function.

Now Variance Minimization itself is an iteration procedure. This is so because $F^2 = \|\boldsymbol{H}\Psi - \lambda^* \cdot \Psi\|^2$ is not only a functional of the wavefunction Ψ but also a function of λ^*. For a fixed wavefunction Ψ, F^2 has its minimum for $\lambda^* = \langle \boldsymbol{H}\Psi|\Psi\rangle$—even though this value may, in reality, be farther away from the eigenvalue than the value of λ^* previously used.

Thus, having obtained a function Ψ_1 minimizing F^2 with respect to a given λ_0^*—say, a Hartree–Fock energy—we may substitute λ_0^* by the energy value $\lambda_1^* := \langle \boldsymbol{H}\Psi_1|\Psi_1\rangle$ of this new function, knowing that even with this function F^2 with respect to this value will be smaller than with respect to the old λ_0^*. We may then find out the function Ψ_2 which minimizes F^2 with respect to this new λ_1^*, substitute λ_1^* by $\lambda_2^* := \langle \boldsymbol{H}\Psi_2|\Psi_2\rangle$ and so on—until Ψ and λ^* do not change any more.

In the case of a Hartree–Fock-like ansatz, this leads to a double iteration procedure:
in an inner iteration loop the occupied orbitals ψ_i are brought to self-consistence with the operator Q defined by them—thus yielding a Slater determinant minimizing F^2 with respect to the given λ^* value;
in the outer loop the previous λ^* is substituted by the energy value of the new function, and the inner loop is entered again with this new λ^*—until λ^* becomes convergent too.

Let us note that the variance expression

$$F^2 = \|\boldsymbol{H}\Psi - \lambda^* \cdot \Psi\|^2$$

will give the exact squared distance between λ^* and an eigenvalue of $\boldsymbol{H}$ only if Ψ is the exact eigenfunction. In any other case the estimate will become all the rougher the poorer the function Ψ is.

This makes it hopeless to expect any useful lower bounds (or good estimates of correlation energies) from a single determinant wavefunction. In fact we shall have to expect a kind of "Hartree–Fock" limit for F^2 that will be much larger than the square of real correlation energy.

In order to provide useful lower bounds, the method will have to be extended e.g. to a Configuration Interaction ansatz. Thus the following calculations can only demonstrate the way the procedure works in the single-determinant case.

2. Numerical calculations

Due to the great demand of computer time and file capacity (note that each element of the matrix Q is a sixfold sum over the basis functions) the method

was only tested for the very simplest closed-shell configurations, namely,

$1s^2$ (He, Be^{2+}) and

$1s^2 2s^2$ (BE).

We used Slater-type basis functions with radial parts

$$R(r) = r^n \cdot \exp(-\alpha \cdot r)$$

with parameters according to Roothaan, Sachs and Weiss [4] and Huzinaga [5], including modified versions of their basis sets.

Solutions of the integrals of these functions in case of atomic systems—including those involving functions with $l \geq 1$—are shown in the Appendix.

The linear combinations of integrals over 1, 2, and 3 electrons' coordinates were computed in advance and catalogued as ready-for-use as possible.

The course of a Roothaan variance minimization procedure for a $1s^2$ system is shown in Table 1.

Table 1. The course of the iteration, He ($1s^2$). Basis set of Roothaan, Sachs, and Weiss (4 basis functions)

Step No. (outer loop)	λ_i^*	Step No. (inner loop)	ε_1	χ_1	E	F^2
$i=1$	−2.86167	1	−0.857	−0.427	−2.7511	0.5556
		2	−1.022	−0.974	−2.8520	0.5341
		3	−0.912	−0.546	−2.7894	0.5276
		4	−0.998	−0.847	−2.8435	0.5216
		5	−0.935	−0.606	−2.8065	0.5192
		6	−0.984	−0.782	−2.8370	0.5173
		7	−0.947	−0.644	−2.8151	0.5164
		8	−0.976	−0.747	−2.8326	0.5158
		9	−0.954	−0.667	−2.8197	0.5155
		10	−0.971	−0.727	−2.8299	—
2	−2.82990	1	−0.955	−0.620	−2.8167	0.5141
		2	−0.972	−0.678	−2.8274	0.5139
		3	−0.959	−0.631	−2.8187	0.5138
		4	−0.970	−0.669	−2.8259	0.5138
		⋮				
3	−2.82385	1	−0.963	−0.635	−2.8209	0.5136
		2	−0.967	−0.648	−2.8233	0.5136
		3	−0.964	−0.638	−2.8213	0.5136
		⋮				
		9	−0.964	−0.641	−2.8219	0.5136
		10	−0.965	−0.644	−2.8225	—
4	−2.82250	1	−0.964	−0.639	−2.8217	0.5136
		2	−0.965	−0.642	−2.8223	0.5136
		3	−0.965	−0.639	−2.8218	0.5136
		4	−0.965	−0.641	−2.8222	0.5136
		⋮				

Table 2. Orbitals filled up in the order of increasing χ_i of increasing ε_i. Be $(1s^2 2s^2)$, six $1s$-type basis functions as in Table 5. The data listed are those of the first inner-loop iteration step for each λ^*. The values of the occupied orbitals are underlined

a) Orbitals filled up in the order of increasing χ_i

Step No. (outer loop)	λ^*	ε_1	χ_1	ε_2	χ_2	ε_3	χ_3	ε_4	χ_4	E	F^2
1	−14.5730	−4.723	−20.224	−0.516	−0.018	−0.044	0.032	0.242	0.365	−14.3038	2.8921
2	−14.4553	−5.038	−23.573	−0.237	−0.045	−0.033	0.031	0.182	0.245	−14.3192	2.8180
3	−14.3687	−5.138	−24.591	−0.203	−0.040	−0.069	0.035	0.120	0.211	−14.2176	2.8025
4	−14.2722	−5.225	−25.463	−0.156	−0.031	−0.088	0.047	0.029	0.197	−14.1014	2.7805
5	−14.1473	−5.312	−26.332	−0.123	−0.020	−0.045	0.063	−0.122	0.215	−14.0146	2.7469
6	−14.0285	−5.375	−26.961	−0.120	−0.010	−0.001	0.073	−0.241!!	0.265	−13.9760	2.7257
7	−13.9781	−5.402	−27.253	−0.121	−0.005	0.007	0.074	−0.289	0.291	−13.9622	2.7223
8	−13.9626	−5.413	−27.373	−0.121	−0.004	0.008	0.073	−0.305	0.298	−13.9576	2.7220
9	−13.9577	−5.416	−27.411	−0.121	−0.004	0.008	0.073	−0.310	0.300	−13.9561	2.7220
10	−13.9561	−5.418	−27.423	−0.121	−0.003	0.008	0.073	−0.312	0.301	−13.9556	2.7220
11	−13.9556	−5.418	−27.427	−0.121	−0.003	0.008	0.073	−0.313	0.301	−13.9554	2.7220

b) Orbitals filled up in the order of increasing ε_i

6	−14.0285	−5.375	−26.961	−0.120	−0.010	−0.001	0.073	−0.241	0.265	−14.2480	3.3303
7	−14.3016	−4.485	−18.118	0.026	0.001	0.030	0.088	0.053	0.362	−14.0134	2.8154
8	−14.1850	−5.289	−26.095	−0.129	−0.024	−0.063	0.059	−0.076	0.205	−14.0334	2.7566
9	−14.0554	−5.362	−26.829	−0.119	−0.012	−0.008	0.071	−0.217	0.251	−14.2246	3.3193

Table 3. Approximation of the Hartree–Fock function for large negative λ^*. Be ($1s^2 2s^2$), Huzinaga basis set (four $1s$-type functions). The data are from *one* step of the outer loop, with $\lambda^* = -10^5$

Step No. (inner loop)	Coefficients of the occupied orbitals Upper line: $1s$; lower: $2s$ $\alpha_1 =$ 6.38280	$\alpha_2 =$ 3.46755	$\alpha_3 =$ 1.77774	$\alpha_4 =$ 0.72619	ε_1 ε_2	χ_1 χ_2	E	F^2	$\lambda^* + \sqrt{F^2}$
Start	−0.121	−1.017	0.171	−0.035	−7.995	—			
	0.192	−1.482	1.481	0.348	−1.961	—	−13.5126	$9.997 \cdot 10^{10}$	−13.5125
1	−0.089	−0.891	−0.035	−0.002	−3.924	−784 627			
	0.003	−0.231	−0.391	1.284	−0.123	−24 630	−14.566 397	$9.997 \cdot 10^{10}$	−14.566 382
2	−0.087	−0.913	−0.012	0.001	−4.697	−939 190			
	−0.011	−0.118	−0.523	1.337	−0.303	−60 612	−14.572 893	$9.997 \cdot 10^{10}$	−14.572 879
3	−0.087	−0.916	−0.009	0.001	−4.728	−945 433			
	−0.014	−0.104	−0.541	1.344	−0.309	−61 693	−14.573 007	$9.997 \cdot 10^{10}$	−14.572 992
4	−0.087	−0.916	−0.009	0.001	−4.732	−946 281			
	−0.014	−0.102	−0.544	1.345	−0.309	−61 825	−14.573 009	$9.997 \cdot 10^{10}$	−14.572 995
⋮									
9	−0.087	−0.916	−0.008	0.001	−4.733	−946 417			
	−0.014	−0.102	−0.544	1.345	−0.309	−61 845	−14.573 009	$9.997 \cdot 10^{10}$	−14.572 995
The data of the corresponding Hartree–Fock function are:									
	−0.087	−0.916	−0.008	0.001	−4.733				
	−0.014	−0.102	−0.544	1.345	−0.309		−14.573 009		

All orbital coefficients with respect to normalized basis functions.

The dates shown are λ_i^* for the ith step of the outer loop, the Lagrange multiplier χ_1 and the orbital energy $\varepsilon_1 = \langle \Psi_1 | F | \Psi_1 \rangle$ for the occupied orbital ψ_1, total energy and F^2 for each step of the inner loop. While F^2 reaches its final value rather quickly, we notice an oscillation not only of the orbital values but also of total energy, which comes to rest only after several steps of the inner iteration loop. After some steps of the outer loop, the oscillations become smaller as the difference between λ^* and $\langle \boldsymbol{H}\Psi | \Psi \rangle$ does.

We have to be aware that the orbitals with lowest χ_i are not necessarily those with lowest orbital energies $\varepsilon_i = \langle i | F | i \rangle$. If in such a case we try to fill the orbitals in the order of increasing ε_i—instead of increasing χ_i—the procedure will not converge any longer; instead, it will be thrown back every now and then to a function with lower total energy, but greater F^2. An example is shown in Table 2.

It has been shown for the case of general Variance Minimization (cf. [3], p. 883), that as the start value of λ^* approaches $-\infty$, the function Ψ achieved in this minimization step will approximate the corresponding Ritz-function, and the upper bound of the variance interval, $\lambda^* + \sqrt{F^2}$ (as well as the energy value of the function) will approach the Ritz energy. In case of a Hartree–Fock-like ansatz this means approximation of the corresponding Hartree–Fock function and energy. As an example for this behavior, such an initial step for Be with $\lambda_0^* = -10^5$ is shown in Table 3 (Huzinaga basis of four 1s-type functions). In this calculation, the eigenvectors of the one-electron hamiltonian matrix H with $H_{ik} = \langle i | H | k \rangle$ were used as start orbitals. The dates of Huzinaga's SCF function are given for comparison.

Table 4. He ($1s^2$)

		a) Basis of Roothaan, Sachs, and Weiss		b) Enlarged basis	
		Orbital coefficients		Orbital coefficients	
n	α	Hartree–Fock	Variance Min.[a]	Hartree–Fock	Variance Min.[a]
0	5.4	—	—	0.000	−0.006
0	3.0	0.175	0.286	0.151	0.044
0	1.4	0.884	0.404	0.964	1.201
1	3.0	0.011	0.072	−0.006	−0.068
1	1.4	−0.051	0.339	−0.122	−0.450
2	1.4	—	—	0.026	0.342
	ε_1	−0.918	−0.965	−0.918	−0.967
	E	−2.861 67	−2.8220	−2.861 679	−2.8125
	λ^*	—	−2.8220	—	−2.8132
	χ_1	—	−0.640	—	−0.657
	F^2	0.5747	0.5136	0.5749	0.5104

[a] Six iteration steps, each with 10 runs of the inner loop. This was not yet sufficient to achieve complete self-consistence, as may be seen by comparing E and λ^*.

All orbital coefficients with respect to normalized basis functions.

Table 5. Be ($1s^2 2s^2$), diverse basis sets

		Huzinaga basis: 4 1s-type functions				Enlarged basis: 6 1s-type functions				Enlarged basis: 5 1s-type, 1 2s-type			
		Hartree–Fock		Variance Min.		Hartree–Fock		Variance Min.		Hartree–Fock		Variance Min.	
n	α	1s	2s	1s	2s	1s	2s	1s	2s	1s	2s	1s	2s
0	6.3828	0.087	−0.014	0.090	−0.022	0.087	−0.014	0.090	−0.001	0.087	0.014	0.090	0.0
0	3.46755	0.916	−0.102	0.858	−0.039	0.916	−0.104	0.857	0.044	0.916	0.104	0.857	0.032
0	1.77774	0.008	−0.544	0.081	−0.650	0.009	−0.538	0.086	−0.193	0.009	0.538	0.086	−0.105
0	0.72619	−0.001	1.345	−0.012	1.387	−0.002	1.290	−0.057	6.783	−0.002	−1.313	−0.047	2.466
0	0.55	—	—	—	—	−0.001	0.117	−0.069	−19.247	—	—	—	—
0	0.45	—	—	—	—	0.000	−0.067	0.028	13.244	—	—	—	—
0	0.30	—	—	—	—	—	—	—	—	0.002	−0.081	0.080	−7.924
1	0.39	—	—	—	—	—	—	—	—	−0.001	0.062	−0.056	7.102
	ε_1	−4.733	−0.309	−4.786	−0.313	−4.733	−0.309	−5.418	−0.120	−4.733	−0.309	−5.430	−0.118
	E	−14.573 009		−14.561 700		−14.573 014		−13.995 413		−14.573 014		−13.946 041	
	λ^*	—		−14.561 700		—		−13.995 431		—		−13.946 068	
	χ_i	—	—	−21.040	0.023	—	—	−27.429	−0.003	—	—	−27.557	−0.004
	F^2	2.979 68		2.906 79		2.979 61		2.721 93		2.979 61		2.720 30	
		(6 "outer"×10 "inner" iteration steps)				(13 "outer"×10 "inner" iteration steps)							

All orbital coefficients with respect to normalized basis functions.

Table 6. Comparison Be^{2+} ($1s^2$)–Be ($1s^22s^2$)

		Be^{2+} Orbital coefficients		Be Orbital coefficients			
		Hartree–Fock	Variance Min.	Hartree–Fock	Variance Min.		
n	α	1s	1s	1s	2s	1s	2s
a) Basis set of Huzinaga							
0	6.3828	0.087	0.090	0.087	−0.014	0.090	−0.022
0	3.46755	0.919	0.861	0.916	−0.102	0.858	−0.039
0	1.77774	0.005	0.076	0.008	−0.544	0.081	−0.650
0	0.72619	−0.000	−0.009	−0.001	1.345	−0.012	1.387
	ε_i	−5.667	−5.695	−4.733	−0.309	−4.786	−0.313
	E	−13.611 297	−13.600 891	−14.573 009		−14.561 700	
	λ^*	—	−13.600 891	—		−14.561 700	
	χ_i	—	−30.485	—	—	−21.040	0.023
	F^2	2.77285	2.70480	2.97968		2.90679	
b) Basis set of Roothaan, Sachs, and Weiss							
0	6.5	0.099	0.129	0.089	−0.076	0.128	−0.059
0	3.4	0.940	0.802	0.935	−0.065	0.805	0.206
0	0.9	0.002	0.018	0.005	0.386	0.018	0.646
1	6.5	−0.009	0.023	0.005	−0.029	0.023	−0.027
1	3.4	−0.025	0.065	−0.023	−0.208	0.064	−0.216
1	0.9	−0.001	−0.009	−0.002	0.741	−0.010	−1.485
	ε_i	−5.667	—	−4.732	−0.309	−4.946	−0.308
	E	−13.611 297	−13.600 734	−14.572 976		−14.499 967	
	λ^*	—	−13.600 734	—		−14.499 968	
	χ_i	—	−30.495	—	—	−22.655	−0.011
	F^2	2.77103	2.70196	2.98097		2.85469	

All orbital coefficients with respect to normalized basis functions.

Tables 4–6 show the results of Variance Minimization calculations for He, Be^{2+}, and Be. As we had to expect, the F^2 values are many times larger than the squares of the correlation energies. Apparently they do not improve very much on improvement of the basis set.

What might seem surprising is that the difference between the variance-minimizing function and the Hartree–Fock function, as well as the difference between the final λ^* value and the Hartree–Fock energy, increases if the basis is enlarged. The energy value of the variance-minimizing function becomes worse for a larger basis!

In former three-particle calculations [6–9] the Ritz and Variance Minimization functions and energy values became more and more similar to each other (as each of them became more and more similar to the true eigenfunction and eigenvalue) if the basis was enlarged.

But these calculations had been carried out in function spaces which allowed to approximate the true wavefunction with arbitrary accuracy. The set of all single-determinant wavefunctions fit for a system does not contain the true wavefunction,

but only a best energy-minimizing Slater determinant (the exact Hartree–Fock function, corresponding to the Hartree–Fock limit as its energy value) and a best variance-minimizing Slater determinant—two different functions approximating the true eigenfunction from different sides. Thus a subset of Slater determinants can only approximate the exact Hartree–Fock function *or* the best variance-minimizing function, but not the true eigenfunction. It is conceivable that the basis sets taken from literature, which had been optimized to approximate the Hartree–Fock function with few basis functions, are not fit to approximate the best variance-minimizing determinant with the same accuracy; thus the variance-minimizing function achieved with this basis remains relatively near to the corresponding Hartree–Fock function. If the basis is improved, the approximation of the best variance-minimizing determinant becomes better too—the F^2 value becomes a little smaller, but λ^* runs farther away from the Hartree–Fock energy.

Table 6 compares results for Be^{2+} $(1s^2)$ with those for Be $(1s^2 2s^2)$. We see that the F^2 values for Be with its 4 electrons are not very much larger than those for Be^{2+}. Although this may partially be due to the basis sets which had been optimized for neutral Be rather than for Be^{2+} (and not for Variance Minimization at all), it seems to indicate that the inaccuracy of the determinantal wavefunctions does mainly come from the inner electrons and that the two additional electrons of neutral Be, in spite of the five new electron–electron interactions they introduce into the atom, contribute comparatively little to total variance.

Appendix

Solutions of integrals needed for Hartree–Fock variance minimization

The calculations have been carried out with Slater-type functions composed of a spherical harmonic and a radial function

$$R_i(r) = r^{n_i} \cdot \exp(-\alpha_i \cdot r).$$

We shall discuss the integrals arising from such functions in the case of atomic systems.

In addition to the types of inner products known from the usual Hartree–Fock procedure,

$$\langle \phi_1 | \phi_2 \rangle, \quad \langle \phi_1 | H | \phi_2 \rangle, \quad \text{and} \quad \langle \phi_1 \phi_2 | \frac{1}{r_{12}} | \phi_3 \phi_4 \rangle,$$

some new products are needed for the calculation of the Q matrix, namely,

$$\langle \phi_1 | H^2 | \phi_2 \rangle, \quad \left\langle \frac{H_1}{r_{12}} \phi_1 \phi_2 \middle| \phi_3 \phi_4 \right\rangle, \quad \langle \phi_1 \phi_2 | \frac{1}{r_{12}^2} | \phi_3 \phi_4 \rangle,$$

and

$$\langle \phi_1 \phi_2 \phi_3 | \frac{1}{r_{12}} \cdot \frac{1}{r_{23}} | \phi_4 \phi_5 \phi_6 \rangle.$$

The first two of these products do not lead to new types of integrals.

Products

$$\langle \phi_1 | H^2 | \phi_2 \rangle$$

give sums of overlap-type integrals, with radial parts of the form

$$\mathcal{R}_0 = \int_0^\infty r^N \exp(-\alpha r)\, dr = N! \alpha^{-N-1}, \qquad \alpha = \alpha_1 + \alpha_2.$$

Products

$$\left\langle \frac{H_1}{r_{12}} \phi_1 \phi_2 \middle| \phi_3 \phi_4 \right\rangle$$

give sums of Coulomb-type integrals, which, by the expansion of $1/r_{12}$ in terms of spherical harmonics [10], decompose into products of a radial part

$$\mathcal{R}_1 = \int_0^\infty \int_0^\infty r_1^{N_1} r_2^{N_2} \cdot r_{<_{12}}^{l_{12}} r_{>_{12}}^{-l_{12}-1} \cdot \exp(-\alpha r_1 - \beta r_2)\, dr_1\, dr_2$$

$$(r_{<_{12}} = \min(r_1, r_2), \quad r_{>_{12}} = \max(r_1, r_2), \quad \alpha = \alpha_1 + \alpha_3, \quad \beta = \alpha_2 + \alpha_4)$$

$$= \sum_{\nu=0}^{N_1 - l_{12} - 1} \frac{(N_1 - l_{12} - 1; -1; \nu)(N_1 + N_2 - \nu - 1)!}{\alpha^{\nu+1} \cdot (\alpha+\beta)^{N_1+N_2-\nu}}$$

$$+ \sum_{\nu=0}^{N_2 - l_{12} - 1} \frac{(N_2 - l_{12} - 1; -1; \nu)(N_1 + N_2 - \nu - 1)!}{\beta^{\nu+1} \cdot (\alpha+\beta)^{N_1+N_2-\nu}} \; *$$

and two integrals of products of three spherical harmonics. New types of integrals arise from products

$$\langle \phi_1 \phi_2 | \frac{1}{r_{12}^2} | \phi_3 \phi_4 \rangle \quad \text{and} \quad \langle \phi_1 \phi_2 \phi_3 | \frac{1}{r_{12}} \cdot \frac{1}{r_{23}} | \phi_4 \phi_5 \phi_6 \rangle.$$

a) Products $\langle \phi_1 \phi_2 | \frac{1}{r_{12}^2} | \phi_3 \phi_4 \rangle$

The operator r_{12}^{-2} is expanded in terms of spherical harmonics in a similar way as the Coulomb operator r_{12}^{-1}. Let x be the cosinus of the angle enclosed by electron 1, nucleus, and electron 2. Then

$$\frac{1}{r_{12}^2} = \frac{1}{r_1^2 + r_2^2 - 2 r_1 r_2 \cdot x} = \frac{1}{r_1^2 + r_2^2} \cdot \frac{1}{1 - \rho \cdot x}$$

with

$$\rho = \frac{2 r_1 r_2}{r_1^2 + r_2^2}.$$

$1/(1-\rho \cdot x)$ is expanded in terms of Legendre polynomials:

$$\frac{1}{1 - \rho \cdot x} = \sum_{l=0}^{\infty} a_l \cdot P_l(x)$$

* $(a; b; n) = a \cdot (a-b) \cdot (a-2b) \cdot \cdots \cdot (n \text{ factors}) \cdot \cdots \cdot (a-(n-1)b)$ ("Kramp's factorial", cf. [11]).

with

$$a_l = \frac{\left\langle \frac{1}{1-\rho x} \middle| P_l(x) \right\rangle}{\|P_l(x)\|^2}$$

$$= \frac{2l+1}{2^{l+1} \cdot l!} \sum_{\nu=0}^{[l/2]} (-1)^\nu \cdot \binom{l}{\nu} \cdot (2l-2\nu; -1; 1) \cdot \int_{-1}^{1} \frac{x^{l-2\nu}}{1-\rho \cdot x}\, dx$$

$$= (2l+1) \cdot 2^{-l-1} \left(\sum_{\nu=0}^{[l/2]} (-1)^\nu \cdot \binom{l}{\nu} \cdot \binom{2l-2\nu}{l} \cdot \rho^{2\nu-l-1} \ln \frac{1+\rho}{1-\rho} \right.$$

$$\left. -2 \sum_{\mu=0}^{[(l-1)/2]} \rho^{-l+2\mu} \cdot \sum_{\nu=0}^{\mu} \frac{(-1)^\nu \cdot \binom{l}{\nu} \cdot \binom{2l-2\nu}{l}}{2\mu-2\nu+1} \right).$$

We resubstitute ρ by $2r_1r_2/(r_1^2+r_2^2)$ and order the sums by ascending powers of r_1 and r_2.

Transcribing the $P_l(x)$ in the expression for $1/r_{12}^2$ into spherical harmonics in θ_1, φ_1, θ_2, and φ_2, we find

$$\frac{1}{r_{12}^2} = \sum_{l_{12}=0}^{\infty} \sum_{m_{12}=-l_{12}}^{l_{12}} \frac{2l_{12}+1}{2} \cdot 4^{-l_{12}} \left(\sum_{k=0}^{l_{12}} r_1^{-l_{12}-1+2k} \cdot r_2^{l_{12}-1-2k} \ln \left| \frac{r_1+r_2}{r_1-r_2} \right| \right.$$

$$\times \sum_{\nu=0}^{k} (-4)^\nu \cdot \binom{l_{12}}{\nu} \cdot \binom{2l_{12}-2\nu}{l} \cdot \binom{l_{12}-2\nu}{k-\nu} - 2 \sum_{k=0}^{l_{12}-1} r_1^{-l_{12}+2k} \cdot r_2^{l_{12}-2k-2}$$

$$\left. \times \sum_{j=0}^{k} 4^{k-j} \cdot \binom{l_{12}-2k+2j-1}{j} \sum_{\nu=0}^{k-j} \frac{(-1)^\nu \cdot \binom{l_{12}}{\nu} \cdot \binom{2l_{12}-2\nu}{l}}{2k-2j-2\nu+1} \right)$$

$$\times \frac{(l_{12}-|m_{12}|)!}{(l_{12}+|m_{12}|)!} P_{l_{12}}^{|m_{12}|}(\cos\theta_1)\, P_{l_{12}}^{|m_{12}|}(\cos\theta_2) \cdot e^{i m_{12}(\varphi_1-\varphi_2)}.$$

By this expansion, products with $1/r_{12}^2$ may be processed like Coulomb products, but with a different radial integral

$$\mathcal{R}_2 = 4^{-l_{12}} \left(\sum_{k=0}^{l_{12}} \int_0^\infty \int_0^\infty r_1^{N_1-l_{12}+2k} \cdot r_2^{N_2+l_{12}-2k} \ln \left| \frac{r_1+r_2}{r_1-r_2} \right| e^{-\alpha r_1-\beta r_2}\, dr_1\, dr_2 \right.$$

$$\times \sum_{j=0}^{k} (-4)^j \cdot \binom{l_{12}}{j} \binom{2l_{12}-2j}{l_{12}} \binom{l_{12}-2j}{k-j}$$

$$- 2 \sum_{k=0}^{l_{12}-1} \int_0^\infty \int_0^\infty r_1^{N_1-l_{12}+2k+1} \cdot r_2^{N_2+l_{12}-2k-1} \cdot e^{-\alpha r_1-\beta r_2}\, dr_1\, dr_2$$

$$\left. \times \sum_{\nu=0}^{k} 4^{k-\nu} \cdot \binom{l_{12}-2k+2\nu-1}{\nu} \cdot \sum_{j=0}^{k-\nu} \frac{(-1)^j \binom{l_{12}}{j} \binom{2l_{12}-2j}{l_{12}}}{2k-2\nu-2j+1} \right).$$

The nonlogarithmic part may be integrated without further processing. In the logarithmic term we substitute

$$\tfrac{1}{2}\cdot(r_1+r_2)=:u,\quad (r_1-r_2)/(r_1+r_2)=:t,$$

$$dr\,dr=2u\,dt\,du.$$

For $\alpha\neq\beta$, integration over du gives (with $N_1+N_2=:N$, $(\alpha+\beta)/(\alpha-\beta)=:C$)

$$\begin{aligned}\mathscr{R}_2^{\neq}=4^{-l_{12}}\Bigg(&\frac{-2(N+1)!}{(\alpha+\beta)^{N+2}}\cdot\sum_{k=0}^{l_{12}}\int_{-1}^{1}\frac{(1+t)^{N_1-l_{12}+2k}\cdot(1-t)^{N_2+l_{12}-2k}}{(t+C)^{N+2}}\ln|t|\,dt\\&\times\sum_{j=0}^{k}(-4)^j\cdot\binom{l_{12}}{j}\binom{2l_{12}-2j}{l_{12}}\binom{l_{12}-2j}{k-j}\\&-2\sum_{k=0}^{l_{12}-1}\frac{(N_1-l_{12}+2k+1)!\,(N_2+l_{12}-2k-1)!}{\alpha^{N_1-l_{12}+2k+2}\cdot\beta^{N_2+l_{12}-2k}}\\&\times\sum_{\nu=0}^{k}4^{k-\nu}\cdot\binom{l_{12}-2k+2\nu-1}{\nu}\cdot\sum_{j=0}^{k-\nu}\frac{(-1)^j\binom{l_{12}}{j}\binom{2l_{12}-2j}{l_{12}}}{2k-2\nu-2j+1}\Bigg).\end{aligned}$$

The integral

$$\mathscr{A}=\int_{-1}^{1}\frac{(1+t)^{N_1-l_{12}+2k}\cdot(1-t)^{N_2+l_{12}-2k}}{(t+C)^{N+2}}\ln|t|\,dt$$

is decomposed to give

$$\begin{aligned}\mathscr{A}=(-1)^{N_2+l_{12}}\cdot&\sum_{\mu=0}^{N}\sum_{\nu=0}^{\mu}(-1)^{\mu}\cdot\binom{N_1-l_{12}+2k}{\mu-\nu}\binom{N_2+l_{12}-2k}{\nu}\\&\times(C-1)^{\mu-\nu}\cdot(C+1)^{\nu}\cdot\int_{-1}^{1}(t+C)^{-\mu-2}\ln|t|\,dt.\end{aligned}$$

The value of the remaining integral is (see [11], No. 322.6b)

$$\begin{aligned}\int_{-1}^{1}(t+C)^{-\mu-2}\ln|t|\,dt=&-\frac{1}{\mu+1}\frac{\ln|t|}{(t+C)^{\mu+1}}\Bigg|_{t=-1}^{1}\\&+\frac{1}{(\mu+1)C^{\mu+1}}\cdot\left(\ln\left|\frac{t}{t+C}\right|+\sum_{\kappa=0}^{\mu}\frac{1}{\kappa}\cdot\left(\frac{C}{C+t}\right)^{\kappa}\right)\Bigg|_{t=-1}^{1}\\=&\frac{1}{(\mu+1)C^{\mu+1}}\cdot\left(\ln\frac{C-1}{C+1}+\sum_{\kappa=1}^{\mu}\frac{1}{\kappa}\cdot\left(\left(\frac{C}{C+1}\right)^{\kappa}-\left(\frac{C}{C-1}\right)^{\kappa}\right)\right).\end{aligned}$$

This is inserted into $\mathscr{R}_2^{\neq}$ to give

$$\begin{aligned}\mathscr{R}_2^{\neq}=4^{-l_{12}}\Bigg\{&\frac{-2(-1)^{N_2+l_{12}}\cdot(N+1)!}{(\alpha-\beta)^{N+2}}\cdot\sum_{\mu=0}^{N}\frac{(-2)^{\mu}}{(\mu+1)(\alpha+\beta)^{\mu+1}}\\&\times\left(\ln\frac{\beta}{\alpha}+\sum_{\kappa=0}^{\mu}\frac{1}{\kappa}\left(\left(\frac{\alpha+\beta}{2\alpha}\right)^{\kappa}-\left(\frac{\alpha+\beta}{2\beta}\right)^{\kappa}\right)\right)\times\sum_{\nu=0}^{\mu}\alpha^{\nu}\cdot\beta^{\mu-\nu}\end{aligned}$$

$$\times \sum_{k=0}^{l_{12}} \sum_{j=0}^{k} (-4)^j \binom{N_1-l_{12}+2k}{\mu-\nu} \binom{N_2+l_{12}-2k}{\nu} \binom{l_{12}}{j} \binom{2l_{12}-2j}{l_{12}} \binom{l_{12}-2j}{k-j}$$

$$-2 \sum_{k=0}^{l_{12}-1} \frac{(N_1-l_{12}+2k+1)!\,(N_2+l_{12}-2k-1)!}{\alpha^{N_1-l_{12}+2k+2} \cdot \beta^{N_2+l_{12}-2k}}$$

$$\times \sum_{\nu=0}^{k} 4^{k-\nu} \cdot \binom{l_{12}-2k+2\nu-1}{\nu} \cdot \sum_{j=0}^{k-\nu} \frac{(-1)^j \binom{l_{12}}{j} \binom{2l_{12}-2j}{l_{12}}}{2k-2\nu-2j+1} \Bigg\}.$$

In the case $\alpha = \beta$, integration over du leads to a much simpler logarithmic term. Integration over dt then leads to

$$\mathscr{R}_2^{=} = 4^{-l_{12}} \Bigg(\frac{4(N+1)!}{(2\alpha)^{N+2}} \cdot \sum_{\mu=0}^{[N/2]} \frac{1}{(2\mu+1)^2} \cdot \sum_{\nu=0}^{2\mu} \sum_{k=0}^{l_{12}} (-1)^\nu$$

$$\times \binom{N_1-l_{12}+2k}{2\mu-\nu} \binom{N_2+l_{12}-2k}{\nu} \sum_{j=0}^{k} (-4)^j \cdot \binom{l_{12}}{j} \binom{2l_{12}-2j}{l_{12}} \binom{l_{12}-2j}{k-j}$$

$$- \frac{2}{\alpha^{N+2}} \cdot \sum_{\mu=0}^{l_{12}-1} \frac{1}{2\mu+1} \cdot \sum_{k=\mu}^{l_{12}-1} (N_1-l_{12}+2k+1)! \cdot (N_2+l_{12}-2k-1)!$$

$$\times \sum_{\nu=0}^{k-\mu} (-1)^\nu \cdot 4^{\mu-\nu} \cdot \binom{l_{12}}{\nu} \binom{2l_{12}-2\nu}{l_{12}} \binom{2l_{12}-2\mu-2\nu-1}{k-\mu-\nu} \Bigg).$$

b) Products $\langle \phi_1\phi_2\phi_3 | \frac{1}{r_{12}} \cdot \frac{1}{r_{23}} | \phi_4\phi_5\phi_6 \rangle$

By multiplication of the expansions of $1/r_{12}$ and $1/r_{23}$ in terms of spherical harmonics, these products decompose into a fourfold sum over l_{12}, m_{12}, l_{23}, and m_{23}.

As in Coulomb-type products, the integrals over the φ coordinates will make all terms vanish except those with certain values of m_{12}, m_{23}. We find

$$m_{12} = m_4 - m_1,$$

$$m_{23} = m_6 - m_3.$$

If $m_1 + m_2 + m_3 \neq m_4 + m_5 + m_6$, the entire product will vanish.

Thus the quadrupole sum reduces to a double one:

$$\left\langle \frac{1}{r_{12}} \phi_1\phi_2\phi_3 \middle| \frac{1}{r_{23}} \phi_4\phi_5\phi_6 \right\rangle = \sqrt{\frac{(2l_1+1)(l_1-|m_1|)! \cdot \cdots \cdot (2l_6+1)(l_6-|m_6|)!}{64 \cdot (l_1+|m_1|)! \cdot (l_2+|m_2|)! \cdot \cdots \cdot (l_6+|m_6|)!}}$$

$$\times \sum_{l_{12}} \sum_{l_{23}} \int_0^\infty \int_0^\infty \int_0^\infty R_1R_4(r_1) \cdot R_2R_5(r_2) \cdot R_3R_6(r_3)$$

$$\times \frac{r_{<12}^{l_{12}} \cdot r_{<23}^{l_{23}}}{r_{>12}^{l_{12}+1} \cdot r_{>23}^{l_{23}+1}} r_1^2 r_2^2 r_3^2 \, dr_1 \, dr_2 \, dr_3$$

$$\times \frac{(l_{12}-|m_{12}|)! \cdot (l_{23}-|m_{23}|)!}{(l_{12}+|m_{12}|)! \cdot (l_{23}+|m_{23}|)!} \int_{-1}^{1} P_{l_1}^{|m_1|} P_{l_{12}}^{|m_{12}|} P_{l_4}^{|m_4|} (\cos\theta_1) \, d\cos\theta_1$$

$$\times \int_{-1}^{1} P_{l_2}^{|m_2|} P_{l_{12}}^{|m_{12}|} P_{l_{23}}^{|m_{23}|} P_{l_5}^{|m_5|} (\cos\theta_2)\, d\cos\theta_2$$

$$\times \int_{-1}^{1} P_{l_3}^{|m_3|} P_{l_{23}}^{|m_{23}|} P_{l_6}^{|m_6|} (\cos\theta_3)\, d\cos\theta_3$$

where l_{12} goes from $|l_1-l_4|$ to l_1+l_4 and l_{23} from $|l_3-l_6|$ to l_3+l_6, each in steps of 2 (for all other values the $d\theta_1$ and $d\theta_3$ integrals are zero). Additionally, terms with $l_{12}+l_{23}<|l_2-l_5|$ or $|l_{12}-l_{23}|>l_2+l_5$ will vanish on account of the $d\theta_2$ integrals (as will be shown later).

We thus have to solve—besides the integrals over three Legendre functions—an integral of a product of 4 Legendre functions and an integral over three radii.

The radial integral

For Slater-type radial functions, the radial integral is

$$\mathscr{R}_3 = \int_0^\infty \int_0^\infty \int_0^\infty r_1^{N_1} r_2^{N_2} r_3^{N_3} \cdot \frac{r_{<12}^{l_{12}} \cdot r_{<23}^{l_{23}}}{r_{>12}^{l_{12}+1} \cdot r_{>23}^{l_{23}+1}}\, e^{-\alpha r_1-\beta r_2-\gamma r_3}\, dr_1\, dr_2\, dr_3$$

where

$$N_1 = \nu_1+\nu_4+2,$$

$$N_2 = \nu_2+\nu_5+2,$$

$$N_3 = \nu_3+\nu_6+2;$$

$$\alpha = \alpha_1+\alpha_4,$$

$$\beta = \alpha_2+\alpha_5,$$

$$\gamma = \alpha_3+\alpha_6.$$

The integral is decomposed into four parts

$$\mathscr{R}_3 = \mathscr{R}_{3\cdot1}+\mathscr{R}_{3\cdot2}+\mathscr{R}_{3\cdot3}+\mathscr{R}_{3\cdot4}$$

with the integration areas

G_1 with $r_1<r_2,\ r_3<r_2$;

G_2 with $r_1<r_2,\ r_2<r_3$;

G_3 with $r_2<r_1,\ r_3<r_2$;

G_4 with $r_2<r_1,\ r_2<r_3$.

In each of the four parts we substitute

$$r_1 =: t\cdot r_2, \qquad r_3 =: u\cdot r_2; \qquad dr_1\, dr_2\, dr_3 = r_2^2\, dt\, du\, dr_2$$

and integrate over dr_2 to achieve

$$\mathscr{R}_{3\cdot1} = \int_0^\infty \int_0^1 \int_0^1 r^N \cdot t^{N_1+l_{12}} \cdot u^{N_3+l_{23}} \cdot e^{-(\beta+\alpha t+\gamma u)r}\, dt\, du\, dr$$

with $N = N_1 + N_2 + N_3$

$$\mathscr{R}_{3\cdot 1} = N! \cdot \int_{u=0}^{1} \int_{t=0}^{1} \frac{t^{N_1+l_{12}} \cdot u^{N_3+l_{23}}}{(\beta+\alpha t+\gamma u)^{N+1}}\, dt\, du;$$

$$\mathscr{R}_{3\cdot 2} = N! \cdot \int_{u=1}^{\infty} \int_{t=0}^{1} \frac{t^{N_1+l_{12}} \cdot u^{N_3-l_{23}-1}}{(\beta+\alpha t+\gamma u)^{N+1}}\, dt\, du;$$

$$\mathscr{R}_{3\cdot 3} = N! \cdot \int_{u=0}^{1} \int_{t=1}^{\infty} \frac{t^{N_1-l_{12}-1} \cdot u^{N_3+l_{23}}}{(\beta+\alpha t+\gamma u)^{N+1}}\, dt\, du;$$

$$\mathscr{R}_{3\cdot 4} = N! \cdot \int_{u=1}^{\infty} \int_{t=1}^{\infty} \frac{t^{N_1-l_{12}-1} \cdot u^{N_3-l_{23}-1}}{(\beta+\alpha t+\gamma u)^{N+1}}\, dt\, du.$$

In the double integrals

$$\mathscr{D} = \iint \frac{t^{M_1} \cdot u^{M_2}}{(\beta+\alpha t+\gamma u)^{N+1}}\, dt\, du$$

we may substitute $\beta+\alpha t+\gamma u =: g$ and $\beta+\alpha t =: h$; then $t = \alpha^{-1} \cdot (h-\beta)$, $u = \gamma^{-1} \cdot (g-h)$, and the integrand decomposes into a polynomial of negative powers of g and positive powers of h:

$$\mathscr{D} = \alpha^{M_1-1} \cdot \gamma^{-M_2-1} \sum_{\mu=0}^{M_1} (-\beta)^{M_1-\mu} \cdot \binom{M_1}{\mu} \cdot \sum_{\nu=0}^{M_2} (-1)^{M_2-\nu} \cdot \binom{M_2}{\nu} \iint g^{\nu-N-1} \cdot h^{M_2+\mu-\nu}\, dg\, dh.$$

By integration over dg we find

$$\begin{aligned}\mathscr{R}_{3\cdot 1} &= \frac{N!}{\alpha^{N_1+l_{12}+1} \cdot \gamma^{N_3+l_{23}+1}} \sum_{\mu=0}^{N_1+l_{12}} (-\beta)^{N_1+l_{12}-\mu} \cdot \binom{N_1+l_{12}}{\mu} \\ &\quad \cdot \sum_{\nu=0}^{N_3+l_{23}} \frac{(-1)^{N_3+l_{23}-\nu}}{\nu-N} \cdot \binom{N_3+l_{23}}{\nu} \\ &\quad \times \left(\int_{\beta}^{\alpha+\beta} h^{N_3+l_{23}+\mu-\nu} \cdot (h+\gamma)^{\nu-N}\, dh - \int_{\beta}^{\alpha+\beta} h^{N_3+l_{23}+\mu-N}\, dh \right) \\ &= \frac{(-1)^{N_1+N_3+l_{12}+l_{23}} N!}{\alpha^{N_1+l_{12}+1} \cdot \gamma^{N_3+l_{23}+1}} \sum_{\mu=0}^{N_1+l_{12}} (-1)^{\mu} \cdot \beta^{N_1+l_{12}-\mu} \cdot \binom{N_1+l_{12}}{\mu} \\ &\quad \sum_{\nu=0}^{N_3+l_{23}} \frac{(-1)^{\nu}}{\nu-N} \cdot \binom{N_3+l_{23}}{\nu} \\ &\quad \times \left(\int_{\beta+\gamma}^{\alpha+\beta+\gamma} (f-\gamma)^{N_3+l_{23}+\mu-\nu} \cdot f^{\nu-N}\, df - \int_{\beta}^{\alpha+\beta} h^{N_3+l_{23}+\mu-N}\, dh \right);\end{aligned}$$

and similarly (with $f = h+\gamma$):

$$\begin{aligned}\mathscr{R}_{3\cdot 2} &= \frac{(-1)^{N_1+N_3+l_{12}-l_{23}} \cdot N!}{\alpha^{N_1+l_{12}+1} \cdot \gamma^{N_3-l_{23}}} \sum_{\mu=0}^{N_1+l_{12}} (-1)^{\mu} \cdot \binom{N_1+l_{12}}{\mu} \cdot \beta^{N_1+l_{12}-\mu} \\ &\quad \sum_{\nu=0}^{N_3-l_{23}-1} \frac{(-1)^{\nu}}{\nu-N} \binom{N_3-l_{23}-1}{\nu} \int_{\beta+\gamma}^{\alpha+\beta+\gamma} (f-\gamma)^{N_3-l_{23}+\mu-\nu-1} \cdot f^{\nu-N}\, df;\end{aligned}$$

$$\mathscr{R}_{3\cdot 3}=\frac{(-1)^{N_1+N_3-l_{12}+l_{23}+1}\cdot N!}{\alpha^{N_1-l_{12}}\cdot\gamma^{N_3+l_{23}+1}}\sum_{\mu=0}^{N_1-l_{12}-1}(-1)^{\mu}\cdot\binom{N_1-l_{12}-1}{\mu}\cdot\beta^{N_1-l_{12}-\mu-1}$$
$$\sum_{\nu=0}^{N_3+l_{23}}\frac{(-1)^{\nu}}{\nu-N}\cdot\binom{N_3+l_{23}}{\nu}$$
$$\times\left(\int_{\alpha+\beta+\gamma}^{\infty}(f-\gamma)^{N_3+l_{23}+\mu-\nu}\cdot f^{\nu-N}\,df-\int_{\alpha+\beta}^{\infty}h^{N_3+l_{23}+\mu-N}\,dh\right);$$

$$\mathscr{R}_{3\cdot 4}=\frac{(-1)^{N_1+N_3-l_{12}-l_{23}+1}\cdot N!}{\alpha^{N_1-l_{12}}\cdot\gamma^{N_3-l_{23}}}\sum_{\mu=0}^{N_1-l_{12}-1}(-1)^{\mu}\binom{N_1-l_{12}-1}{\mu}\cdot\beta^{N_1-l_{12}-\mu-1}$$
$$\cdot\sum_{\nu=0}^{N_3-l_{23}-1}\frac{(-1)^{\nu}}{\nu-N}\cdot\binom{N_3-l_{23}-1}{\nu}\int_{\alpha+\beta+\gamma}^{\infty}(f-\gamma)^{N_3-l_{23}+\mu-\nu-1}f^{\nu-N}\,df.$$

The four parts are mixed up, the summands ordered in terms of equal integrals, and integrated to give

$$\mathscr{R}_3=\frac{(-1)^{N_1+N_3+l_{12}+l_{23}}\cdot N!}{\alpha^{N_1+l_{12}+1}\cdot\gamma^{N_3+l_{23}+1}}\cdot\sum_{\mu=0}^{N_1+l_{12}}\sum_{\nu=0}^{N_3+l_{23}}\frac{(-1)^{\mu+\nu}}{\nu-N}$$
$$\Bigg\{-\alpha^{2l_{12}+1}\cdot\beta^{N_1-l_{12}-\mu-1}\cdot\binom{N_1-l_{12}-1}{\mu}\binom{N_3+l_{23}}{\nu}\cdot\frac{(\alpha+\beta)^{N_3+l_{23}+\mu-N+1}}{N_3+l_{23}+\mu-N+1}$$
$$-\beta^{N_1+l_{12}-\mu}\cdot\binom{N_1+l_{12}}{\mu}\binom{N_3+l_{23}}{\nu}$$
$$\begin{cases}\dfrac{(\alpha+\beta)^{N_3+l_{23}+\mu-N+1}}{N_3+l_{23}+\mu-N+1}-\dfrac{\beta^{N_3+l_{23}+\mu-N+1}}{N_3+l_{23}+\mu-N+1}\\ \quad\text{(in case } N_3+l_{23}+\mu-N\neq-1\text{) or—respectively—}\\ \ln(\alpha+\beta)-\ln\beta\\ \quad\text{(in case } N_3+l_{23}+\mu-N=-1)\end{cases}$$
$$+\sum_{j=0}^{N_3+l_{23}+\mu-\nu}(-\gamma)^{N_3+l_{23}+\mu-\nu-j}\left(\binom{N_3+l_{23}}{\nu}\binom{N_3+l_{23}+\mu-\nu}{j}\right.$$
$$\left.-\binom{N_3-l_{23}-1}{\nu}\binom{N_3-l_{23}+\mu-\nu-1}{j}\right)$$
$$\begin{cases}\beta^{N_1+l_{12}-\mu}\cdot\binom{N_1+l_{12}}{\mu}\\ \quad\begin{cases}\dfrac{(\alpha+\beta+\gamma)^{\nu+j-N+1}}{\nu+j-N+1}-\dfrac{(\beta+\gamma)^{\nu+j-N+1}}{\nu+j-N+1}\\ \quad\text{(in case } \nu+j-N\neq-1\text{) or—respectively—}\\ \ln(\alpha+\beta+\gamma)-\ln(\beta+\gamma)\\ \quad\text{(in case } \nu+j-N=-1)\end{cases}\\ +\alpha^{2l_{12}+1}\cdot\beta^{N_1-l_{12}-\mu-1}\cdot\binom{N_1-l_{12}-1}{\mu}\dfrac{(\alpha+\beta+\gamma)^{\nu+j-N+1}}{\nu+j-N+1}\end{cases}\Bigg\}$$

Integrals of four Legendre functions

We have to solve integrals

$$\int_{-1}^{1} P_k^{|t|} P_l^{|u|} P_m^{|v|} P_n^{|w|} (\cos\theta)\, d\cos\theta$$

where the sum of the upper indices, $t+u+v+w$, is zero. (The sum of the lower indices must be even in this case; otherwise the integrand would become antisymmetric.)

The following deductions are made for integrals of arbitrarily many Legendre functions with zero sum of the upper indices. We may write such an integral as

$$\begin{aligned}\mathcal{W} &= \int_{-1}^{1} P_{m_1}^{u_1} \cdot \cdots \cdot P_{m_\mu}^{u_\mu} \cdot P_{n_1}^{|v_1|} \cdot \cdots \cdot P_{n_\nu}^{|v_\nu|}(x)\, dx \\ &= \frac{2^{-\Sigma m_i - \Sigma n_j}}{m_1! \cdots n_\nu!} \times \int_{-1}^{1} (1-x^2)^{(\Sigma u_i + \Sigma |v_j|)/2} \cdot \frac{d^{m_1+u_1}}{dx^{m_1+u_1}} (x^2-1)^{m_1} \cdot \cdots \\ &\quad \cdot \frac{d^{n_\nu+|v_\nu|}}{dx^{n_\nu+|v_\nu|}} (x^2-1)^{n_\nu}\, dx\end{aligned}$$

where the u_i are positive (or zero), the v_i negative (or zero). The sum of the u_i is equal to the sum of the $|v_i|$. Thus

$$(1-x^2)^{(\Sigma u_i + \Sigma |v_j|)/2} = (1-x^2)^{\Sigma u_i} = (1-x^2)^{\Sigma |v_j|}$$

and by the relation (see [12])

$$(1-x^2)^{|v_j|} \cdot \frac{d^{n_j+|v_j|}}{dx^{n_j+|v_j|}} (x^2-1)^{n_j} = (n_j+|v_j|; -1; 2|v_j|) \cdot \frac{d^{n_j-|v_j|}}{dx^{n_j-|v_j|}} (x^2-1)^{n_j}$$

we may use the $(1-x^2)^{\Sigma |v_j|}$ up to transform the integral into

$$\begin{aligned}\mathcal{W} &= \frac{2^{-\Sigma m_i - \Sigma n_j}}{m_1! \cdots n_\nu!} \cdot (n_1+|v_1|; -1; 2|v_1|) \cdot \cdots \cdot (n_\nu+|v_\nu|; -1; 2|v_\nu|) \qquad (*) \\ &\quad \times \int_{-1}^{1} \frac{d^{m_1+u_1}}{dx^{m_1+u_1}} (x^2-1)^{m_1} \cdot \cdots \cdot \frac{d^{m_\mu+u_\mu}}{dx^{m_\mu+u_\mu}} (x^2-1)^{m_\mu} \\ &\quad \cdot \frac{d^{n_1-|v_1|}}{dx^{n_1-|v_1|}} (x^2-1)^{n_1} \cdot \cdots \cdot \frac{d^{n_\nu-|v_\nu|}}{dx^{n_\nu-|v_\nu|}} (x^2-1)^{n_\nu}\, dx.\end{aligned}$$

Integration of this polynomial gives

$$\begin{aligned}\mathcal{W} &= \frac{(n_1+|v_1|; -1; 2|v_1|) \cdot \cdots \cdot (n_\nu+|v_\nu|; -1; 2|v_\nu|)}{2^{\Sigma m_i + \Sigma n_j} \cdot m_1! \cdot \cdots \cdot n_\nu!} \\ &\quad \times \sum_{i_1=0}^{[(m_1-u_1)/2]} \cdots \sum_{i_\mu=0}^{[(m_\mu-u_\mu)/2]} \sum_{j_1=0}^{[(n_1+|v_1|)/2]} \cdots \sum_{j_\nu=0}^{[(n_\nu+|n_\nu|)/2]} (-1)^{i_1+\cdots+j_\nu} \\ &\quad \times \binom{m_1}{i_1} \cdot \cdots \cdot \binom{m_\mu}{i_\mu} \binom{n_1}{j_1} \cdot \cdots \cdot \binom{n_\nu}{j_\nu}\end{aligned}$$

$$\times(2m_1-2i_1;-1;m_1+u_1)\cdot\cdots\cdot(2m_\mu-2i_\mu;-1;m_\mu+u_\mu)$$
$$\times(2n_1-2j_1;-1;n_1-|v_1|)\cdot\cdots\cdot(2n_\nu-2j_\nu;-1;n_\nu-|v_\nu|)$$
$$\times\frac{2}{m_1+\cdots+n_\nu-2i_1-\cdots-2j_\nu+1}$$

$$=2\frac{(n_1-v_1;-1;2|v_1|)\cdot\cdots\cdot(n_\nu-v_\nu;-1;2|v_\nu|)}{2^{\sum m_i+\sum n_j}\cdot m_1!\cdot\cdots\cdot n_\nu!}$$
$$\times\sum_{\kappa=0}^{k/2}\frac{(-1)^\kappa}{k-2\kappa+1}\sum_{i_2=0}^{[m_2-u_2/2]}\cdots\sum_{i_\mu=0}^{[m_\mu-u_\mu/2]}\sum_{j_1=0}^{[(n_1-v_1)/2]}\cdots\sum_{j_\nu=0}^{[(n_\nu-v_\nu)/2]}$$
$$\times\binom{m_1}{\kappa-i_1-\cdots-j_\nu}\cdot\binom{m_2}{i_2}\cdot\cdots\cdot\binom{m_\mu}{i_\mu}\cdot\binom{n_1}{j_1}\cdot\cdots\cdot\binom{n_\nu}{j_\nu}$$
$$\times(2m_1-2\kappa+2i_2+\cdots+2j_\nu;-1;m_1+u_1)$$
$$\times(2m_2-2i_2;-1;m_2+u_2)\cdot\cdots\cdot(2m_\mu-2i_\mu;-1;m_\mu+u_\mu)$$
$$\times 2n_1-2j_1;-1;n_1+v_1)\cdot\cdots\cdot(2n_\nu-2j_\nu;-1;n_\nu+v_\nu)$$

(with $k=\sum m_i+\sum n_j$); the latter formula has the advantage that the inner loops are integer.

Expression (*) may be used to deduce an extension of Gaunt's triangle rule [13]: integrals of the kind treated here are zero if any of the lower indices is greater than the sum of the others.

To prove this, expression (*) is integrated partially integrating up one factor

$$\frac{d^{n_k-|v_k|}}{dx^{n_k-|v_k|}}(x^2-1)^{n_k}.$$

The integral functions of this factor are zero for $x=\pm1$; the remaining integral is

$$\mathcal{W}=\frac{2^{-\sum m_i-\sum n_j}}{m_1!\cdots n_\nu!}\cdot(n_1+|v_1|;-1;2|v_1|)\cdot\cdots\cdot(n_\nu+|v_\nu|;-1;2|v_\nu|)$$
$$\times\int_{-1}^{1}(x^2-1)^{n_k}\cdot\frac{d^{n_k-|v_k|}}{dx^{n_k-|v_k|}}\left\{\frac{d^{m_1+u_1}}{dx^{m_1+u_1}}(x^2-1)^{m_1}\cdot\cdots\cdot\frac{d^{m_\mu+u_\mu}}{dx^{m_\mu+u_\mu}}(x^2-1)^{m_\mu}\right.$$
$$\left.\cdot\frac{d^{n_1-|v_1|}}{dx^{n_1-|v_1|}}(x^2-1)^{n_1}\cdot\cdots\cdot\binom{\text{omit the}}{k\text{th factor}}\cdot\cdots\frac{d^{n_\nu-|v_\nu|}}{dx^{n_\nu-|v_\nu|}}(x^2-1)^{n_\nu}\right\}dx.$$

This will vanish if the degree of the polynomial in braces—which is to be derivated $(n_k-|v_k|)$ times—is less than $n_k-|v_k|$.

The degree of this polynomial is

$$\sum_i m_i+\sum_{j\neq k}n_j-\sum_i u_i+\sum_{j\neq k}|v_j|.$$

Thus $\mathcal{W}$ will vanish if not

$$\sum_i m_i + \sum_{j\neq k} n_j - \sum_i u_i + \sum_{j\neq k} |v_j| \geq n_k - |v_k|$$

$$\sum_i m_i + \sum_{j\neq k} n_j - \sum_i u_i + \sum_j |v_j| \geq n_k$$

$$\sum_i m_i + \sum_{j\neq k} n_j \geq n_k \quad \text{for any } n_k.$$

(The same may be shown for the m_i if we use the $(1-x^2)^{\sum u_i}$ to transform the $P_{m_i}^{u_i}$ instead of the $P_{n_j}^{|v_j|}$.)

In the present case, the rule gives an additional restriction of the possible values of l_{12} and l_{23}, namely,

$$l_{12}+l_{23} \geq |l_2 - l_5| \quad \text{and} \quad |l_{12}-l_{23}| \geq l_2 + l_5.$$

References

1. Pauli, G., Kleindienst, H.: Theor. Chim. Acta (Berl.) (1984)
2. Kleindienst, H.: Untersuchungen über das Spektrum von Schrödinger-Operatoren. Habilitation thesis, Düsseldorf 1975
3. Kleindienst, H., Altmann, W.: Int. J. Quant. Chem. **10**, 873 (1976)
4. Roothaan, C. C. J., Sachs, L. M., Weiss, A. W.: Rev. Mod. Phys. **32**, 186 (1960)
5. Huzinaga, S.: J. Chem. Phys. **67**, 5973 (1977)
6. Kleindienst, H., Baumgarten, E., Altmann, W.: Int. J. Quant. Chem. **10**, 887 (1976)
7. Kleindienst, H., Müller, W.: Theoret. Chim. Acta (Berl.) **56**, 183 (1980)
8. Kleindienst, H., Pauli, G., Müller, W.: Theoret. Chim. Acta (Berl.) **59**, 451 (1981)
9. Pauli, G.: Ein Analogon zum Hartree–Fock–Roothaan–Verfahren bei Verwendung des Varianzminimierungsprinzips. Dissertation, Düsseldorf 1983
10. Eyring, H., Walter, J., Kimball, G.: Quantum chemistry Appendix V, pp. 369 ff. New York: Wiley 1970
11. Gröbner, W., Hofreiter, N.: Integraltafel 1. Teil. Wien/New York: Springer-Verlag 1965
12. Lense, J.: Reihenentwicklungen in der mathematischen Physik, p. 156 f. Berlin: W. de Gruyter & Co. 1953
13. Gaunt, J. A.: Philosophical Transactions of the Royal Society of London, Appendix, pp. 192 ff. **A228**, 151 (1929)

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