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On the optimisation of exponents of *d* and *f* polarisation functions for first row atoms*

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Summary. The theory of Kutzelnigg and Klopper, which introduces the interelectronic co-ordinates into the first order Møller–Plesset wavefunction, requires diagonal matrix elements of the operators:

$$\left\{r_{12} \times \frac{1}{r_{12}} - 1\right\}$$

and

$$\left\{r_{12} \times \frac{\boldsymbol{r}_{12} \cdot (\nabla_1 - \nabla_2)}{4r_{12}} + \frac{3}{4}\right\}.$$

These are evaluated through completeness insertions, and used to obtain corrections to pair energies which vanish as the one-particle basis set becomes complete. We suggest optimising exponents of *d* and *f* polarisation functions to minimise these corrections, and have obtained 1*d*, 2*d*, 3*d* and 1*f* sets for B, C, N, O, F and Ne. These are compared with other sets reported in the literature.

Key words: *d* and *f* polarisation functions – Optimisation of exponents – Electron correlation

1 Introduction

There are two motivations for this work. Firstly, we have examined in some detail the theory of Kutzelnigg and Klopper (KK) [2–10] which introduces the interelectronic distance r_{12} explicitly into the first order Møller–Plesset wavefunction. Secondly, we have been aware for some time that the exponents of polarisation functions which are commonly used today (such as the "*" in '6-31G*' [11, 12] and 'P' in 'DZP' [13, 14]) were not developed for correlated wavefunctions. In this paper, we are suggesting the use of aspects of the KK theory to optimise these exponents [15].

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* Submitted in honour of Professor K. Ruedenberg, recognising in particular his introduction of the idea of even-tempered basis sets [1]

The essential KK theory is given in Sect. 2. It involves writing the first order Møller–Plesset wavefunction as the usual double replacement term, together with an extra term derived from $r_{12}\Phi_0$, where Φ_0 is the SCF wavefunction. The second order energy is minimised, and the difficult three- and four-electron integrals are evaluated through insertion of the resolution of the identity using the one-particle basis set. In other words, it is assumed that the one-particle basis set is complete:

$$\sum_{p}^{\text{all}} |\phi_p(1)\rangle\langle\phi_p(1)| = 1. \tag{1}$$

However, it is not assumed that the product $\phi_p(1)\phi_q(2)$ is a complete two-particle basis and this incompleteness arises explicitly in the formula for the correction to the pair energies f_{ij} for the occupied orbitals ϕ_i and ϕ_j. Specifically:

$$f_{ij} = e_{ij} + \frac{V_{ij}^2}{V_{ij} - U_{ij}} \tag{2}$$

where e_{ij} are the usual pair MP2 pair energies and:

$$V_{ij} = \frac{1}{2} - \frac{1}{2}\sum_{p<q} \langle[\phi_i\phi_j]|r_{12}|[\phi_p\phi_q]\rangle\langle[\phi_p\phi_q]|\frac{1}{r_{12}}|[\phi_i\phi_j]\rangle, \tag{3}$$

$$U_{ij} = \frac{3}{4} + \frac{1}{4}\sum_{p<q} \langle[\phi_i\phi_j]|r_{12}|[\phi_p\phi_q]\rangle\langle[\phi_p\phi_q]|\frac{(\mathbf{r}_{12}\cdot(\nabla_1 - \nabla_2))}{r_{12}}|[\phi_i\phi_j]\rangle. \tag{4}$$

In these expressions, $[\phi_i\phi_j]$ denotes an antisymmetric product. We can see that Eq. (3) is a diagonal matrix element of the operator:

$$\left\{r_{12} \times \frac{1}{r_{12}} - 1\right\} \tag{5}$$

and Eq. (4) is the corresponding expression for:

$$\left\{r_{12} \times \frac{\mathbf{r}_{12}\cdot(\nabla_1 - \nabla_2)}{4r_{12}} + \frac{3}{4}\right\}, \tag{6}$$

where the two-particle completeness expression has been inserted.

The success of the KK theory depends upon the fact that, as the basis set is enlarged, U_{ij} and V_{ij} tend to zero, and in the limit of a complete basis set f_{ij} is equal to e_{ij}. Furthermore, the remaining error in f_{ij} as complete shells of increasing angular momentum quantum number are added to the basis set goes as $(l + 1)^{-5}$; if only e_{ij} is considered, the error increments as $(l + 1)^{-3}$. This is shown by KK [9, 10] and demonstrated by ourselves [16] with calculations on Ne, HF and H_2O. If we take Ne as an example (Table 1), we find that $U\ (=\sum U_{ij})$ and $V\ (=\sum V_{ij})$

Table 1. Calculations on Ne (taken from ref. [16]) using extended basis sets, demonstrating how the values of V and U decrease as the basis set is enlarged

Basis set	$-E_{\text{SCF}} + 128$	$-E_{\text{MP2}}$	$-E_{\text{MP2-R12}}$	V	U
8*s*8*p*[a]	0.5465	0.1912	0.6527	1.23	3.20
8*s*8*p*5*d*	0.5466	0.3171	0.4068	0.13	0.09
8*s*8*p*5*d*3*f*	0.5466	0.3520	0.3881	0.05	0.02

[a] [52111111]*s*8*p* contraction of the 13*s*8*p* primitive set of Van Duijneveldt, ref. [24]

are good measures of the completeness of the basis set for these correlated wavefunctions, and this suggests that we choose basis sets which minimise these quantities and make the regular pair energies as reliable as possible. It has been known for a long time that it requires a far larger basis set for $\phi_p(1)\phi_q(2)$ to be a near complete two-particle basis than for $\phi_p(1)$ to be a near complete one-particle basis and this is shown by the large number of functions required to reach the *spdf* limits for U and V, which completely cover the SCF requirement.

Historically, polarisation function exponents for first row atoms were chosen for SCF calculations. The 6-31G* basis sets were optimised for a selection of small molecules [12]. That these functions were important in allowing atomic orbitals to distort in a molecular environment was demonstrated in calculations of the inversion barrier of NH_3 [17, 18], for which *d* functions on the nitrogen are almost entirely responsible [18].

If a single *d* set is used, the basis may only be good enough for a reasonable SCF calculation, although circumstances oblige many to use these sets for correlated studies, and the suitability of these exponents is then questionable. Prescriptions have been given for generating larger sets by appropriate splitting of the 1*d* exponent [19], but we believe that a different approach should be used.

This problem was addressed by Dunning [10], who optimised sets of 3*d*2*f*1*g* functions in CISD calculations on first row atoms. This was part of an attempt to obtain compact basis sets of the same quality as those developed by Almlöf and Taylor [21] using atomic natural orbitals. (This scheme makes it possible to use polarisation spaces which are effectively saturated by using a general contraction scheme, allowing all primitives of a given type to contribute to each contracted function.)

In Sect. 3 we compare our exponents with those obtained by Dunning, and others in common use. We have also calculated valence MP2 energies for CH_4, NH_3, H_2O, HF and Ne with our new polarisation sets and compare them with energies obtained using older sets, and we suggest that our exponents are reasonable for correlated studies on molecules containing first row atoms.

2 Theory

2.1 The MP2-R12 method

Kutzelnigg and Klopper begin with the Hylleraas variational principle:

$$E^{(2)} \leqslant \langle \Psi^{(1)} | H^{(0)} - E^{(0)} | \Psi^{(1)} \rangle + 2 \langle \Psi^{(1)} | H^{(1)} - E^{(1)} | \Psi^{(0)} \rangle \tag{7}$$

for the energy in second order Møller–Plesset pertubation theory (MP2). They argue that the main deficiency of a first order wavefunction ψ_1 expanded in a finite one-electron basis is its failure to obey the electron-electron cusp condition as the interelectronic distance r_{ij} tends to zero. Therefore they consider a first order wavefunction for the *ij* electron pair constructed from the SCF reference determinant with the spin orbitals ϕ_i and ϕ_j replaced by u_{ij}:

$$u_{ij}(1,2) = \frac{1}{2} c_{ij} \{1 - P(1)\}\{1 - P(2)\} r_{12} [ij] + \sum_{a,b} d_{ij}^{ab} [ab]. \tag{8}$$

Here,

$$P(1) = \sum_k |\phi_k(1)\rangle\langle\phi_k(1)| \tag{9}$$

is a projection operator which ensures that the first term in Eq. (8) is always orthogonal to the reference pair:

$$\langle u_{ij}(1,2)|[ij]\rangle = 0, \tag{10}$$

c_{ij} and d_{ij}^{ab} are linear variational parameters and:

$$[ij] = \frac{1}{\sqrt{2}}[\phi_i(1)\phi_j(2) - \phi_j(1)\phi_i(2)]. \tag{11}$$

They substitute Eq. (8) into the Hylleraas expression (7) for the ij pair energy to give:

$$2\langle[ij]|\frac{1}{r_{ij}}|u_{ij}(1,2)\rangle + \langle u_{ij}(1,2)|F(1)+F(2)-\epsilon_i-\epsilon_j|u_{ij}(1,2)\rangle. \tag{12}$$

An exact evaluation of this expression requires the evaluation of three- and four-electron integrals. Kutzelnigg and Klopper avoid this, and evaluate Eq. (12) approximately by assuming that ϕ_i and ϕ_j are the exact eigenfunctions of the Fock operator F and that the orbital set $\{\phi_p\}$ is complete in the one-electron space:

$$1 = \sum_p |\phi_p(1)\rangle\langle\phi_p(1)| \equiv Q(1). \tag{13}$$

The result of inserting these assumptions into Eq. (12) is that the pair energy consists of the regular MP2 pair energy:

$$-\sum_{a<b}\frac{[(ai|bj)-(bj|ai)]^2}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j}, \tag{14}$$

and

$$\sum_{k=1}^{3}\langle[ij]|r_{12}[1-Q(1)Q(2)]A_k|[ij]\rangle \tag{15}$$

where

$$A_1 = \left(c_{ij}-\frac{1}{2}c_{ij}^2\right)\frac{1}{r_{12}} \tag{16a}$$

$$A_2 = -\frac{1}{4}c_{ij}^2\frac{\mathbf{r}_{12}\cdot(\nabla_1-\nabla_2)}{r_{12}} \tag{16b}$$

$$A_3 = -\frac{1}{4}c_{ij}^2[K(1)+K(2), r_{12}]. \tag{16c}$$

$K(1)$ is the exchange operator in $F(1)$. The evaluation of the A_3 term in Eq. (16c), involving three-electron integrals, is much more difficult than the evaluation of the A_1 and A_2 terms. If it is ignored, the pair energy f_{ij} is given by:

$$f_{ij} = e_{ij} + (2c_{ij}-c_{ij}^2)V_{ij} + c_{ij}^2U_{ij} \tag{17}$$

where e_{ij} is the conventional MP2 pair energy and:

$$V_{ij} = \frac{1}{2}-\frac{1}{2}\sum_{p<q}\langle[ij]|r_{12}|[pq]\rangle\langle[pq]|\frac{1}{r_{12}}|[ij]\rangle \tag{18}$$

$$U_{ij} = \frac{3}{4}+\frac{1}{4}\sum_{p<q}\langle[ij]|r_{12}|[pq]\rangle\langle[pq]|\frac{(\mathbf{r}_{12}\cdot(\nabla_1-\nabla_2))}{r_{12}}|[ij]\rangle. \tag{19}$$

Finally, optimising f_{ij} with respect to c_{ij} gives:

$$f_{ij} = e_{ij} + c_{ij} V_{ij} \tag{20}$$

where

$$c_{ij} = \frac{V_{ij}}{(V_{ij} - U_{ij})}. \tag{21}$$

This is a stable procedure, because it turns out that V_{ij} and U_{ij} have opposite signs, at least for the cases considered so far. This is related to the fact that exact asymptotic values exist for c_{ij}, implying such relationships between V_{ij} and U_{ij}.

Both Eqs. (18) and (19) involve completeness relations such that V_{ij} and U_{ij} tend to zero as the one-electron basis set becomes complete. Turning this around suggests that regular pair energies e_{ij} become more accurate as V_{ij} and U_{ij} are reduced in magnitude. We have shown [16] that, as the basis sets become complete, V_{ij} and U_{ij} do tend to zero and the e_{ij} become almost exact. Therefore, we argue that a given finite basis set will be most reliable when the exponents are chosen to minimise these quantities.

2.2 Exponent optimisation

V_{ij} and U_{ij} are both independent of the orbital energies ϵ_i. This means that we can estimate the completeness of basis sets used in open shell calculations by forming V and U from the orbitals produced by an ROHF calculation. We undertook such calculations for first row atoms, starting with an $8s8p$ basis set shown to be effectively complete in our previous study. Core electrons were not included, and the remaining electron pairs weighted according to the number of possible spin orientations.

We added polarisation functions with exponents in the following sequence:

$$\alpha_{1d}$$

$$\alpha_{2d}, \alpha_{2d}\beta_{2d}$$

$$\alpha_{3d}, \alpha_{3d}\beta_{3d}, \alpha_{3d}\beta_{3d}^2$$

$$\alpha_{3d}, \alpha_{3d}\beta_{3d}, \alpha_{3d}\beta_{3d}^2, \alpha_{1f}$$

This imposes an even-tempered restriction [1] on the $3d$ set, meaning that the exponents form a geometric sequence. (This was the procedure used by Dunning [20], and Davidson and Feller [22] in their optimisation of $3d$ sets at the CISD level.) In each case, α and β were optimised by calculating a grid of points around the minimum. For the $1d$ function, this involved a single quadratic interpolation on a grid of $\Delta\alpha = 0.1$. Where two parameters were involved, a steplength of $\Delta\beta = 0.5$ was used, and the minimum obtained from a two-dimensional spline representation of the surface. All cartesian components of the d and f functions were used.

Finally, we draw attention to Appendix B of Ref. [10], in which KK describe their prescription for choosing optimum polarisation functions, assuming that the SCF orbitals may be represented by a single dominant basis function. Our work is similar to the KK prescription, but uses the complete SCF orbitals.

Table 2. Values of $1d$ exponents obtained by minimisation of (i) V (Eq. (18)) and (ii) U (Eq. (19)) using an $8s8p1d$ basis set, compared with literature values

	(i) V	(ii) U	Dunning[a]	Ahlrichs/Taylor[b]	6311G*[c]	631G*[d]	Amos[e]	Feller[f]
B	0.37	0.32	0.34	0.50	0.40	0.70	0.70	
C	0.57	0.50	0.55	0.72	0.63	0.80	0.80	0.55
N	0.85	0.74	0.82	0.98	0.91	0.80	0.80	0.80
O	1.13	1.03	1.19	1.28	1.29	0.80	0.90	1.20
F	1.47	1.35	1.64	1.62	1.75	0.80	1.20	
Ne	1.86	1.72	2.20	2.00	2.30			

[a] ref. [20]
[b] ref. [25]
[c] ref. [26]
[d] ref. [12]
[e] ref. [29]
[f] ref. [22]

3 Results and discussion

3.1 Exponents

The $1d$ sets obtained by minimising both U and V separately are given in Table 2. We observe that

(i) The U-optimised sets have slightly smaller exponents than the V-optimised sets.

(ii) The V- and U-sets are closer to the Dunning [20] set than any other. We might expect this, because it can be argued that both approaches are related to the optimisation of the correlation energy. The Dunning exponents are very close to those obtained by Feller [22] for C, N, and O.

(iii) The Ahlrichs/Taylor [25] set has larger exponents for all atoms except Ne.

(iv) The SCF optimised sets, 6-31G* [12] and Amos [29], do not show as much variation as those sets determined from correlated calculations.

The $2d$ sets are shown in Table 3. We note that

(i) Excluding B, the larger of the two exponents in the V and U sets is larger than the corresponding exponent in the other published sets.

(ii) Again, the closest agreement to be between the V- and U-optimised sets and the Dunning set.

The $3d$ sets are shown in Table 4. It is seen that there is close agreement between the U-optimised set and those of Dunning [20], and Feller [22], although the largest of the three exponents in the U set is larger than that of Dunning. The V-optimised exponents are somewhat larger than those optimised with respect to U.

Our optimised $1f$ exponents are shown in Table 5. There is a good agreement between the V-optimised $1f$ set and the Dunning set, although the U set is not significantly different.

Table 3. Values of 2*d* exponents obtained by minimisation of (i) *V* (Eq. (18)) and (ii) *U* (Eq. (19)) using an 8*s*8*p*2*d* basis set, compared with literature values

	(i) *V*	(ii) *U*	Dunning[a]	Amos[b]	Feller[c]
B	0.21, 0.82	0.15, 0.80	0.20, 0.66	0.35, 1.05	
C	0.33, 1.39	0.24, 1.23	0.32, 1.10	0.40, 1.20	0.34, 1.16
N	0.47, 2.08	0.35, 1.80	0.47, 1.65	0.45, 1.35	0.48, 1.68
O	0.61, 2.75	0.45, 2.46	0.65, 2.31	0.45, 1.35	0.67, 2.47
F	0.79, 3.57	0.56, 3.22	0.86, 3.20	0.67, 2.00	
Ne	0.99, 4.54	0.70, 4.07	1.10, 4.01	0.80, 2.40	

[a] ref. [20]
[b] ref. [29]
[c] ref. [22]

Table 4. Values of 3*d* exponents obtained by minimisation of (i) *V* (Eq. (18)) and (ii) *U* (Eq. (19)) using an 8*s*8*p*3*d* basis set, compared with literature values

	(i) *V*	(ii) *U*	Dunning[a]	Feller[b]
B	0.17, 0.54, 1.80	0.12, 0.46, 1.84	0.15, 0.40, 1.11	
C	0.24, 0.83, 2.88	0.17, 0.66, 2.57	0.23, 0.65, 1.85	0.31, 0.96, 2.98
N	0.34, 1.20, 4.23	0.24, 0.93, 3.65	0.34, 0.97, 2.84	0.32, 0.94, 2.74
O	0.43, 1.54, 5.52	0.30, 1.24, 5.14	0.44, 1.30, 3.78	0.44, 1.26, 3.56
F	0.54, 1.97, 7.23	0.36, 1.54, 6.59	0.59, 1.173, 5.01	
Ne	0.68, 2.47, 9.05	0.45, 1.92, 8.32	0.75, 2.21, 6.47	

[a] ref. [20]
[b] ref. [22]

Table 5. Values of 1*f* exponents obtained by minimisation of (i) *V* (Eq. (18)) and (ii) *U* (Eq. (19)) using an 8*s*8*p*3*d*1*f* basis set, compared with literature values

	(i) *V*	(ii) *U*	Dunning[a]	Feller[b]
B	0.53	0.43	0.49	
C	0.80	0.69	0.76	0.76
N	1.15	1.02	1.09	1.06
O	1.54	1.39	1.43	1.35
F	2.00	1.78	1.92	
Ne	2.54	2.27	2.54	

[a] ref. [20]
[b] ref. [22]

3.2 MP2 energies for small molecules

We have now used our optimised *d* exponents in conjunction with 4*s*2*p* and 5*s*4*p* sets to calculate the SCF and valence MP2 energies of CH_4, NH_3, H_2O, HF and Ne. Results are presented in Tables 6 and 7.

Table 6. Calculations on CH_4, NH_3, H_2O, HF and Ne at the experimental geometries[a] using 4*s*2*p*1*d* basis sets with the 1*d* exponents given in Table 2

	CH_4[b]	NH_3	H_2O	HF	Ne	
Ahlrichs[c]	40.2078	56.2082	76.0455	100.0472	128.5238	$-E_{SCF}$
	0.1594	0.1853	0.2002	0.1976	0.1770	$-E_{MP2(valence)}$
Dunning[d]	40.2053	56.2073	76.0466	100.0475	128.5240	
	0.1615	0.1873	0.2021	0.1985	0.1776	
Amos[e]	40.2076	56.2082	76.0465	100.0479		
	0.1595	0.1862	0.1977	0.1934		
4*s*2*p*1*d*(*V*)	40.2071	56.2082	76.0463	100.0477	128.5326	
	0.1608	0.1864	0.2007	0.1972	0.1760	
4*s*2*p*1*d*(*U*)	40.2065	56.2080	76.0463	100.0478	128.5234	
	0.1598	0.1856	0.1999	0.1960	0.1741	

[a] taken from ref. [10]: HF: $R_e = 1.7328\,a_0$ H_2O: $R_e = 1.80885\,a_0, \alpha = 104.52°$ NH_3: $R_e = 1.91240\,a_0, \alpha = 106.72°$ CH_4: $R_e = 2.05227\,a_0$

[b] for H, $\alpha_p = 1.0$

[c] ref. [25]

[d] ref. [20]

[e] ref. [29]

In Table 6, Dunning's 4*s*2*p* segmented contraction [13] of Huzinaga's 9*s*5*p* primitive set [28] is used throughout. The 1*d* exponents are those given in Table 2. For H, a [4*s*/2*s*] basis with exponents scaled by 1.2 is used, to which a set of *p* functions with exponent of 1.0 has been added.

We see that there is less than 0.002 Hartrees variation in the SCF energies given by these 4*s*2*p*1*d*, sets, with the Dunning CH_4 energy being most out of line. For the MP2 energies, we see that the Dunning set gives the largest absolute correlation energy for all of these molecules, but the correlation energies given by the *V*-optimised set are at most 0.0014 Hartrees smaller. The *U*-optimised set gives correlation energies ~0.001 Hartrees smaller than those obtained with the *V*-optimised set. The Amos set correlation energies are certainly inferior for H_2O and HF, which is presumably due to the *d* exponents for O and F being too small.

Table 7. Calculations on CH_4, NH_3, H_2O, HF and Ne at the experimental geometries using 5*s*4*p*2*d* basis sets with the 2*d* exponents given in Table 3

	CH_4[a]	NH_3	H_2O	HF	Ne	
Amos[b]	40.2138	56.2182	76.0604	100.0633	128.5359	$-E_{SCF}$
	0.1856	0.2201	0.2407	0.2512	0.2408	$-E_{MP2(valence)}$
Dunning[c]	40.2138	56.2182	76.0604	100.0633	128.5367	
	0.1847	0.2202	0.2455	0.2555	0.2485	
5*s*4*p*2*d*(*V*)	40.2137	56.2178	76.0599	100.0630	128.5368	
	0.1848	0.2194	0.2441	0.2541	0.2469	
5*s*4*p*2*d*(*U*)	40.2138	56.2178	76.0599	100.0630	128.5368	
	0.1829	0.2177	0.2413	0.2497	0.2412	

[a] for H, $\alpha_p = 1.5, 0.5$

[b] ref. [29]

[c] ref. [20]

The results obtained using $5s4p2d$ quality basis sets are given in Table 7. All used Dunning's $5s4p$ segmented contraction [27] of the $10s6p$ primitive set of Huzinaga [28] with the $2d$ exponents taken from Table 3. The H basis is $[5s/3s]$ with p functions having exponents (0.5, 1.5).

As expected, there is a much smaller variation in the SCF energies, with the largest being a 0.0008 Hartrees deficiency in the Amos energy for Ne. However, for the correlation energy there is a much greater variation, with 0.008 in the Ne results. Except for CH_4, the Dunning set gives the largest correlation energies; the $5s4p2d(V)$ correlation energies are close to these, the largest difference being 0.0016 for Ne. The $5s4p2d(U)$ optimised sets give the smallest correlation energies overall.

From these limited results we observe that the energies given by our V-optimised sets are in close agreement with the results obtained using the Dunning basis, which give the largest correlation energies overall. This method is therefore an alternative procedure by which optimised orbital exponents can be obtained. The fact that it is V, a simpler generator than U, which gives the best results means that the method is attractive to use because the integrals involving the r_{12} operator are easily obtained from $1/r_{12}$ integrals [16]. The method may therefore be used to optimise exponents for molecules as well as atoms, if this is desirable.

It is perhaps interesting to finish with a comparison of the two methods for obtaining optimised exponents:

(i) Here, we have suggested that the quantity:

$$\sum_{ij}\left\{\sum_{p<q}\langle[ij]|r_{12}|[pq]\rangle\langle[pq]|\frac{1}{r_{12}}|[ij]\rangle - 1\right\} \tag{22}$$

is minimised.

(ii) If the MP2 pair energies are optimised (which is an approximation to the Dunning approach, then:

$$\sum_{ij}\sum_{a<b}\frac{\langle[ij]|H|[ab]\rangle\langle[ab]|H|[ij]\rangle}{\epsilon_a+\epsilon_b-\epsilon_i-\epsilon_j} \tag{23}$$

is maximised.

From our calculations, it appears that the two approaches give very similar results. Indeed, this follows because $1/r_{12}$ is related to the commutator $[F, r_{12}]$.

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