

Rate of Convergence of the Partial Wave Expansion of Atomic States. Unnatural Parity States. Hund's Rules

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The configuration interaction (CI) and the partial wave expansion (PWE) for two-electron systems

Like any n -electron wave function, that for $n = 2$ can be expanded in the n -electron Slater determinants constructable from the given one-electron basis. However, for $n = 2$, space and spin can be completely separated, and the wave function is either a symmetric function in space multiplied by an antisymmetric spin function (for a *singlet state*) or vice versa (for a *triplet state*).

The spatial wave function for a singlet can then be expanded in products of spinfree orbitals:

$$\Psi(1, 2) = \sum_{k,l} c_{k,l} \{ \varphi_k(\vec{r}_1) \varphi_l(\vec{r}_2) + \varphi_k(\vec{r}_2) \varphi_l(\vec{r}_1) \} \quad (1)$$

A spinfree two-electron wave function for an atom in an 1S -state can be written as $\psi(r_1, r_2, r_{12})$ and can be expanded in a **partial wave expansion**, i.e. in **Legendre polynomials** of the cosine of the angle $\vartheta \equiv \vartheta_{12}$ between the electronic position vectors \vec{r}_1 and \vec{r}_2

$$\psi(\vec{r}_1, \vec{r}_2) = \sum_{l=0}^{\infty} \psi_l(r_1, r_2) P_l(\cos \vartheta) \quad (2)$$

Closely related to an expansion in one-electron states. Expand further:

$$\psi_l(r_1, r_2) P_l(\cos \vartheta) = \frac{4\pi}{2l+1} \sum_{p,q} c_{pq} \varphi_{lp}(r_1) \varphi_{lq}(r_2) \sum_{m=-l}^l Y_l^m(\vartheta_1, \varphi_1) Y_l^{m*}(\vartheta_2, \varphi_2) \quad (3)$$

The l^{th} term in the PWE (2) is equal to the contribution of one-electron functions with **angular quantum number l** in a **CI-type expansion** of ψ .

The formulas of Schwartz and Hill

C. Schwartz [1] was the first to study the rate of convergence of the expansion of correlated wave functions in a one-electron basis. Perturbative treatment of the He ground state, with the bare nuclear Hamiltonian as H_0 and the electron interaction as the perturbation.

The first order wave function ψ expanded in a PWE (2),

$$H_0 = \frac{1}{2}\nabla_1^2 - \frac{1}{2}\nabla_2^2 - \frac{Z}{r_1} - \frac{Z}{r_2}; \quad V = r_{12}^{-1}; \quad E_1 = \langle \phi | V | \phi \rangle \quad (4)$$

$$(H_0 - E_0)\phi = 0; \quad (H_0 - E_0)\psi = -(V - E_1)\phi \quad (5)$$

$$E_2 = \sum_{l=0}^{\infty} E_l^{(2)}; \quad E_l^{(2)} = \langle \phi | V | \psi_l P_l \rangle = \langle \phi | V_l P_l^2 | \psi_l \rangle \quad (6)$$

$$\psi = \sum_{l=0}^{\infty} \psi_l P_l(\cos \theta); \quad V = \sum_{l=0}^{\infty} V_l P_l(\cos \theta); \quad V_l = \frac{r_{<}^{l-1}}{r_{>}^l} \quad (7)$$

Partial wave increments $E_l^{(2)}$ obey the asymptotic formula [1]

$$E_l^{(2)} = -\frac{45}{256}\left(l + \frac{1}{2}\right)^{-4} + \frac{225}{1024}\left(l + \frac{1}{2}\right)^{-6} + O\left(\left[l + \frac{1}{2}\right]^{-8}\right) \quad (8)$$

Perturbation expansion of the energies of all ions isoelectronic with He:

$$E = Z^2\left(E_0 + \frac{1}{Z}E_1 + \frac{1}{Z^2}E_2 + \frac{1}{Z^3}E_3 + \dots\right) \quad (9)$$

($1/Z$ -expansion) first proposed by [Hylleraas](#) [2, 3] easily derived by appropriate scaling ($\vec{r} \rightarrow \vec{r}/Z$) in (4), (5).

Schwartz's derivation is based on the fact that the exact wave function displays a correlation cusp (Kato) [4] which implies that the 1st order wave function behaves for small r_{12} as

$$\psi = (1 + \frac{1}{2}r_{12})\phi + O(r_{12}^2) \quad (10)$$

$$\psi_k \sim \frac{1}{2}(r_{12})_k\phi; (r_{12})_k = \frac{1}{2l+3} \frac{r_{<}^{l+2}}{r_{>}^{l+1}} - \frac{1}{2l-1} \frac{r_{<}^l}{r_{>}^{l-1}} \quad (11)$$

where ϕ is the unperturbed (zeroth-order) wave function. The correlation cusp itself is a direct consequence of the singularity of the Coulomb interaction r_{12}^{-1} at $r_{12} = 0$.

More recently Hill [5], taking up prior work by Klahn and Morgan [6], studied the rate of convergence of variational calculations from a semi-rigorous mathematical point of view (making some very plausible, but unproven assumptions on the exact wave function)

One of his examples was the partial wave expansion of the Helium ground state, for which he showed that the error ΔE_L of a *variational calculation* in a basis truncated at some angular quantum number L goes as

$$\Delta E_L = C_1(L + 1)^{-3} + C_2L^{-4} + O(L^{-5}) \quad (12)$$

C_1 and C_2 are expressible in terms of the wave function $\Psi(r_1, r_2, r_{12})$ of the ground state of He

$$C_1 = 2\pi^2 \int_0^\infty |\Psi(r, r, 0)|^2 r^5 dr \quad (13)$$

$$C_2 = \frac{12\pi}{5} \int_0^\infty |\Psi(r, r, 0)|^2 r^6 dr \quad (14)$$

Hill's [5] result implies that the partial wave increments due to basis functions with a given l in a CI calculation are asymptotically proportional to $(l + \frac{1}{2})^{-4}$, like the partial wave increments to $E^{(2)}$ studied by Schwartz, just with a different coefficient.

This behavior of a CI expansion had been conjectured by Lakin [7] and had been demonstrated in a numerical calculation of the ground state of He by Carroll et al. [8], which led to very pessimistic conclusions as to the applicability of CI to accurate calculations.

A $(l + \frac{1}{2})^{-4}$ behavior of the partial wave increments also holds in perturbation theory based on the Hartree-Fock-Hamiltonian as H_0 , again with a different coefficient [9].

Generalizations to arbitrary states of two-electron atoms were derived by Kutzelnigg and Morgan [9]. To prepare this, we must first have a careful look at the cusp condition for **general two-electron systems**.

The generalized correlation cusp for two-electron systems

We now consider the solution of the Schrödinger equation near $r_{12} = 0$ explicitly for a *two-electron system*, and we separate off the spin. The eigenfunctions can then be classified

(a) as *singlet or triplet* depending on **symmetry** or **antisymmetry** with respect to exchange of \vec{r}_1 and \vec{r}_2

(b) as *gerade (g) or ungerade (u)* depending on symmetry or antisymmetry with respect to $\vec{r}_k \rightarrow -\vec{r}_k$

(c) by the **total angular momentum** \mathcal{L}

(d) as of *natural* or *unnatural parity* [9]. Since for one-electron states l even always corresponds to *gerade* parity and l odd to *ungerade* parity, while for n -electron states *any* l can be associated with overall *gerade* or *ungerade* parity, it does make sense to define that a state has **natural parity**, if its parity is equal to $(-1)^L$, and **unnatural parity**, if the parity of the state is equal to $(-1)^{(L+1)}$. So S_g, P_u, D_g etc. have natural parity, S_u, P_g, D_u have unnatural parity.

We express the spinfree wave function Ψ of a two electron system in terms of **center-of-mass and relative coordinates** \vec{R} and \vec{r} of the two electrons.

$$\Psi(\vec{R}, \vec{r}); \quad \vec{R} = \frac{1}{2}(\vec{r}_1 + \vec{r}_2); \quad \vec{r} = \vec{r}_1 - \vec{r}_2 \quad (15)$$

$$\Psi(-\vec{R}, -\vec{r}) = \pm \Psi(\vec{R}, \vec{r}); \quad +\text{for gerade}, -\text{for ungerade states} \quad (16)$$

$$\Psi(\vec{R}, -\vec{r}) = \pm \Psi(\vec{R}, \vec{r}); \quad +\text{for singlet}, -\text{for triplet states} \quad (17)$$

We expand Ψ in spherical harmonics of the center of mass and relative coordinates

$$\vec{R} = (R, \Theta, \phi); \quad \vec{r} = (r, \vartheta, \varphi) \quad (18)$$

$$\Psi = \sum_{L, M} \sum_{k, m} \Psi_{Lk}^{Mm}(R, r) Y_L^M(\Theta, \phi) Y_k^m(\vartheta, \varphi) \quad (19)$$

Obviously

$$L \text{ even, } k \text{ even} \quad \text{for singlet gerade} \quad (20)$$

$$L \text{ odd, } k \text{ even} \quad \text{for singlet ungerade} \quad (21)$$

$$L \text{ odd, } k \text{ odd} \quad \text{for triplet gerade} \quad (22)$$

$$L \text{ even, } k \text{ odd} \quad \text{for triplet ungerade} \quad (23)$$

L and k couple to the total angular momentum \mathcal{L} . We have

$$\begin{aligned} \mathcal{L} - L - k \text{ even} & \quad \text{for natural parity states} \\ \mathcal{L} - L - k \text{ odd} & \quad \text{for unnatural parity states} \end{aligned} \quad (24)$$

This leads to the classification

$$\text{natural parity singlet} \quad : k \text{ even}, \mathcal{L} - L \text{ even} \quad (25)$$

$$\text{natural parity triplet} \quad : k \text{ odd}, \mathcal{L} - L \text{ odd} \quad (26)$$

$$\text{unnatural parity singlet} \quad : k \text{ even}, \mathcal{L} - L \text{ odd} \quad (27)$$

$$\text{unnatural parity triplet} \quad : k \text{ odd}, \mathcal{L} - L \text{ even} \quad (28)$$

The minimum allowed even/odd k is 0/1 respectively; however, $k = 0$ is impossible for $\mathcal{L} - L$ odd. Hence the leading partial waves in the relative coordinate are

$$k = 0 \text{ for natural parity singlet states} \quad (29)$$

$$k = 1 \text{ for arbitrary triplet states} \quad (30)$$

$$k = 2 \text{ for unnatural parity singlet states} \quad (31)$$

We now consider the Schrödinger equation at $r_{12} \equiv r \rightarrow 0$

$$\left[-\frac{1}{2r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{k(k+1)}{2r^2} + \frac{\lambda}{r} + O(r^0) \right] \Psi_k^m(\vec{R}, \vec{r}) = 0 \quad (32)$$

In order to satisfy (32) Ψ_k must behave as

$$\Psi_k^m(\vec{R}, \vec{r}) \sim \left\{ r^k \left(1 + \frac{\lambda}{2(k+1)} r \right) + O(r^{k+2}) \right\} Y_k^m(\vartheta, \varphi) \quad (33)$$

For natural-parity singlet states where the leading partial wave of the relative motion is that with $k = 0$, (33) is essentially Kato's correlation cusp condition. For triplet states with $k = 1$ (33) implies the generalized cusp condition [10], while the result with $k = 2$ for natural parity singlet states has only rather recently been found by Morgan and Kutzelnigg [9, 11, 12].

Figure 1: Schematic plot of the Coulomb hole (upper curve), the Fermi hole (middle curve) and the hole for unnatural-parity singlet states (lower curve). The wavefunction is displayed as function of r_{12} .

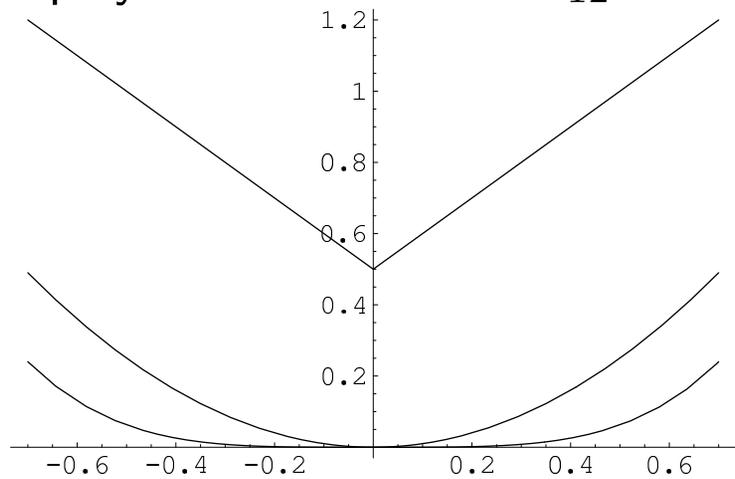


Table 1: PWE of $E^{(2)}$ of He-like ions, for quantum numbers n_1, l_1, n_2, l_2, L

natural parity singlet	$-\frac{3}{8}NR_+^{(5)}F_0\{(l+\frac{1}{2})^{-4}-\frac{5}{4}(l+\frac{1}{2})^{-6}\}$
natural parity triplet	$-N\left\{\frac{5}{64}F_0R_-^{(7)}+\frac{15}{256}(F_1-G_1)R_+^{(5)}\right\}(l+\frac{1}{2})^{-6}$
unnatural parity triplet	$-\frac{15}{128}NF_1R_+^{(5)}(l+\frac{1}{2})^{-6}$
unnatural parity singlet	$-N\left\{\frac{35}{384}F_1R_-^{(7)}+\frac{77}{3072}(F_2-G_2)R_+^{(5)}\right\}(l+\frac{1}{2})^{-8}$
$N = (1 + \delta_{n_1 n_2} \delta_{l_1 l_2})^{-1}$	$J = (-1)^L (2l_1 + 1)(2l_2 + 1)$
$R_+^{(5)} = \int_0^\infty \varrho_+(r, r) r^5 dr;$	$\varrho_\pm(r, r') = \frac{1}{2} R_1(r)R_2(r') \pm R_2(r)R_1(r') ^2$
$R_-^{(7)} = \int_0^\infty \varrho'_-(r, r) r^7 dr;$	$\varrho'_-(r, r') = \partial^2[\varrho_-(r, r')]/\partial r'^2$
$F_p = J \sum_{n=0}^{2\min(l_1, l_2)} (2n+1)[n(n+1)]^p$	$\left\{ \begin{matrix} l_1 & l_1 & n \\ & l_2 & L \end{matrix} \right\} \begin{pmatrix} l_1 & l_1 & n \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2 & n \\ 0 & 0 & 0 \end{pmatrix}$
$G_p = J \sum_{n= l_1-l_2 }^{l_1+l_2} (2n+1)[n(n+1)]^p$	$\left\{ \begin{matrix} l_1 & l_2 & n \\ & l_2 & L \end{matrix} \right\} \begin{pmatrix} l_1 & l_2 & n \\ 0 & 0 & 0 \end{pmatrix}^2$
$F_0 = G_0 = (2l_1+1)(2l_2+1)$	$\begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2$
Expressions like $\begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}$ and $\left\{ \begin{matrix} l_1 & l_2 & n \\ & l_2 & L \end{matrix} \right\}$ are Wigner $3j$ and $6j$ symbols	

Table 2: Numerical values of the coefficients of $(l + \frac{1}{2})^{-n}$ of the 2^{nd} order energy (in the $1/Z$ expansion) for states of the He isoelectronic series

state	$n =$	4	6	8
$^1S_g(1s^2)$	-	0.17578125	0.21972656	
$^1S_g(1s2s)$	-	0.04115226	0.05144033	
$^3S_g(1s2s)$		0.0	- 0.06001372	
$^1P_u(1s2p)$	-	0.09602195	0.12002744	
$^3P_u(1s2p)$		0.0	- 0.02667276	
$^1D_g(1s3d)$	-	0.00486660	0.00608325	
$^3D_g(1s3d)$		0.0	- 0.00601988	
$^3P_g(2p3p)$		0.0	- 0.18811699	
$^1P_g(2p3p)$		0.0	0.0	- 1.25536739
$^1D_u(2p3d)$		0.0	0.0	- 0.09012894
$^1D_u(3p3d)$		0.0	0.0	0.76076507
$^3D_u(2p3d)$		0.0	- 0.41385738	
$^1F_u(2p3d)$	-	0.28378792	0.35473490	
$^3F_u(2p3d)$		0.0	- 0.08750128	
$^1F_g(2p4f)$		0.0	0.0	- 0.19227989
$^3F_g(2p4f)$		0.0	- 0.06054294	

Convergence of the partial wave expansion

Kutzelnigg and Morgan [9] have derived the leading terms of the PWE contributions to the second (and also third order) in Z^{-1} for general states of atoms isoelectronic with He. The second-order results are summarized in table 2, with the corresponding numerical values in table 3.

To illustrate table 2 we consider the $(1s)^1S$ ground state of He-like ions, that has already been studied long ago by Schwartz [1]. Here one has

$$\begin{aligned} N &= \frac{1}{2}, \quad F_0 = 1; \quad R_1(r) = R_2(r) = 2Z^{3/2}e^{-Zr}; \quad \varrho_+(r) = 32Z^6e^{-4Zr} \\ R_+^{(5)} &= 32 \int_0^\infty Z^6 e^{-4Zr} r^5 dr = \frac{15}{16} \end{aligned} \quad (34)$$

and the value for the coefficient of $(l + \frac{1}{2})^{-4}$ is $-\frac{45}{256}$, in agreement with (8).

The most noteworthy message of this study [9] is that the leading term is of $O([l + \frac{1}{2}]^{-4})$ only for *natural-parity singlet states*, it is of $O([l + \frac{1}{2}]^{-6})$ for *triplet states of either natural or unnatural parity* (but with a different origin in the two cases), and it is of $O([l + \frac{1}{2}]^{-8})$ for *unnatural-parity singlet states*.

To second order in perturbation theory in Z^{-1} only even orders in $([l + \frac{1}{2}]^{-1})$ arise. Odd orders in $([l + \frac{1}{2}]^{-1})$ appear in third and higher orders in Z^{-1} , and are therefore present in Hill's result [5] for the nonexpanded wave function.

The generalization to many-electron systems involves the two-particle density matrices [9].

Evaluation of the asymptotically leading terms

From the PWE of r_{12} and r_{12}^{-1} one gets factors like

$$\frac{r_{<}^{2k}}{r_{>}^{2k}} \quad (35)$$

in the integrals. These peak at $r_1 = r_2$ and allow a Taylor expansion around $r_1 = r_2$. Further manipulation is possible via integration by parts.

Wave functions with explicit r_{ij} dependence. Hylleraas-CI.

Use variational trial wave functions that depend explicitly on the interelectronic distances r_{ij} , in particular that contain terms **linear** in the r_{ij} and allow to describe the correlation cusp correctly.

Hylleraas obtained an excellent variational energy for the ground state of He-like ions with a compact ansatz $\Psi(r_1, r_2, r_{12})$ with only a small number of parameters. This was improved by **Kinoshita** [14], while the elaborate calculation by **Pekeris** [15] remained a landmark for quite some time.

A similar ansatz for the H₂-molecule by **James and Coolidge** [16] and mainly **Kolos and Wolniewicz** [17, 18, 19, 20].

Generalization to n -electron systems has been prohibited by the need to evaluate many-electron integrals of the type (and even more complicated ones).

$$\int f_1(\vec{r}_1) f_2(\vec{r}_2) \dots r_{12} r_{13} r_{23}^{-1} d^3 r_1 d^3 r_2 d^3 r_3 \quad (36)$$

The evaluation of each single integral is quite time consuming, but even more problematic is the large number of these integrals. Only rather recently some progress has been achieved for 3- and-electron atoms [21, 22, 23, 24, 26, 27]. It is unlikely that Hylleraas-CI has a serious chance to be practicable for systems with more than, say, 4 electrons.

In atomic calculations one can – alternatively to r_{12} , with some success, use $r_<$ and $r_>$, i.e. the smaller and the greater of r_1 and r_2 (with a generalization to n -electron systems) as independent variables [28].

Traditional CI-type calculations in a one-electron basis do not allow a high accuracy, because of the slow convergence with the basis size, while calculations like Hylleraas CI that allow a fast convergence in principle, are impracticable, except for very small systems.

The R12-method

The basic idea of R12 method [29, 30, 31] is to combine a **conventional CI-like basis expansion** approach like MP2 or CC with the inclusion of terms that take care of the **linear r_{ij} dependence** of the wave function near the coalescence of two electrons.

One starts from a single Slater determinant reference function Φ with the orbitals φ_I occupied, and one constructs *additional n -electron basis functions*, obtained from Φ on replacing an orbital pair $\varphi_I(1)\varphi_J(2)$ by a pair function

$$r_{12}\varphi_I(1)\varphi_J(2) \quad (37)$$

and includes these additional n -electron basis functions in a variational calculation.

Actually one uses different pair functions for singlet and triplet pairs, and one even includes pair functions, in which $\varphi_K(1)\varphi_L(2)$ is replaced by (37) (with K, L different from I, J) [32].

In practice one first orthogonalizes these pair functions to the *excited* Slater determinants that one includes in the CI part, such that the remaining pair functions correct for the *incompleteness of the one-electron basis* to describe the correlation cusp.

An essential feature of the R12 method is that **only two-electron integrals** are needed. However, in addition to the classical electron repulsion integrals

$$\langle \varphi_p(1)\varphi_q(2) | r_{12}^{-1} | \varphi_r(1)\varphi_s(2) \rangle \quad (38)$$

one also needs

$$\langle \varphi_p(1)\varphi_q(2) | r_{12} | \varphi_r(1)\varphi_s(2) \rangle \quad (39)$$

$$\langle \varphi_p(1)\varphi_q(2) | [T, r_{12}] | \varphi_r(1)\varphi_s(2) \rangle \quad (40)$$

An essential ingredient of the R12 method is the **systematic introduction of completeness insertions** in such a way that (i) 3- and 4-electron integrals don't arise explicitly, (ii) the results become **exact in the limit of a complete one-electron basis**, (iii) the basis truncation error decreases much faster with the size of the basis than in conventional calculations, such that **much higher accuracy is achieved with less computational effort**. The only disadvantage is that no strict upper-bond property holds, but this is not even the case for conventional coupled-cluster calculations. There is no stronger limitation of the size of the system to be computed than for conventional CC calculations.

A certain drawback is that relatively large basis sets have to be used, they should be **sufficiently close to complete** for the *low angular momenta*, i.e. essentially for s, p, d , and to some extent f . This can be avoided if one introduces an *auxiliary basis* to satisfy completeness relations, while for the actual calculations a smaller basis can be used [33]. If one includes explicit linear r_{12} -dependent terms in the wave functions and expands only the remainder [29], **the l -increments of the remainder go essentially as $(l + \frac{1}{2})^{-8}$** , at least at the level of 2^{nd} order perturbation theory, which is a substantial improvement.

It is somewhat surprising that in the R12 method there appears **no need for a *damping*** of the r_{12} factor for large r_{12} . It appears that on one hand the decay of the one-electron functions, and on the other hand the linear variational coefficient, takes care of this to a sufficient extent.

Gaussian geminals

An alternative to the use of linear r_{ij} -terms as in the R12 method, is the method of *Gaussian geminals*. Here one introduces correlation factors of the form

$$\exp(-\gamma r_{12}^2) \quad (41)$$

With such functions it is *not possible to satisfy the correlation cusp exactly*, but all integrals that arise, including three and four-electron integrals, can be evaluated in closed form. The convergence of this kind of expansion is much faster than that of a CI (or a partial-wave expansion), but by far not as fast as Hylleraas-CI. It is possibly similar to that of the expansion of a $1s$ hydrogen wave function in a Gaussian basis.

Recently [Rychlewski](#) and coworkers [34] have been able to achieve for the ground state of the He atom a similar accuracy as Pekeris [15] even with a wave function of Gaussian geminal type

$$\Psi = \sum_i c_i \exp(-\alpha_{1i}|\vec{r}_1 - \vec{A}_i|^2 - \alpha_{2i}|\vec{r}_2 - \vec{B}_i|^2 - \beta_i(|\vec{r}_1 - \vec{r}_2|^2)). \quad (42)$$

For He 12-figure accuracy was reported [34, 35]. This is surprising since this ansatz neither fulfills the nuclear cusp nor the correlation cusp conditions. Although it is not yet fully understood why this works, some preliminary comments can be made.

The Gaussian geminal method has been implemented for many-electron atoms or molecules in combination with e.g. MP2 and CCSD [36]. A rather difficult practical problem is that of the **choice of the optimum non-linear parameters γ** . This has so far inhibited the application of the Gaussian geminal method beyond HF [37] or H₂O [38]. The technique of Rychlewski et. al. [34] to optimize non-linear parameters has to the authors' knowledge not yet been applied in this context.

Exact extrapolations to the basis limit

If one is able to compute the individual partial wave increments E_l to the energy accurately, and knows at the same time the correct asymptotic expansion of these increments, one can combine these two sources of information in an effective way.

Take as an example the 2^{nd} order energy $E^{(2)}$ of the ground state of He-like ions in the $1/Z$ expansion. We know that in view of (8) the truncation error of $E^{(2)}$ – for limiting the series at $l = L$ is given as

$$\Delta E_L^{(2)} = \frac{15}{256}(L+1)^{-3} - \frac{45}{1024}(L+1)^{-5} + O([L+1]^{-7}) \quad (43)$$

Using this formula we can estimate that $L = 38$ is required to get an accuracy of 1 microhartree from a brute force partial wave expansion. Let us now assume that we calculate some truncated $E_L^{(2)}$, but correct it for the first term of the truncation error (43). Then the error is dominated by the second term of (43). To make this remaining error smaller than 1 microhartree we need only $L = 8$.

If we correct also for the second term the maximum required L is reduced to $L = 6$. This means that it is sufficient to obtain the partial wave increments for $l = 0, 1, 2, \dots, 6$ in order to obtain $E^{(2)}$ accurate to 1 microhartree, provided that one knows the coefficients in the asymptotic error formula (43). This is confirmed by taking the partial-wave increments up to $l = 6$ from Schmidt and Hirschhausen [39], which sum to $-157499.67 \mu E_h$; the first term in (1.11) corrects this to $-157670.49 \mu E_h$, and the second to $-157667.88 \mu E_h$, compared with the exact value [40] of $157666.43 \mu E_h$.

Of course, this procedure requires that the **low partial wave increments are sufficiently accurate**, since errors in them cannot be corrected by the asymptotic error formula.

Numerical extrapolations

If one is able to evaluate the partial wave increments E_l for low l , but does *not* know the exact asymptotic behavior of the E_l , one can try to extrapolate numerically.

This is **dangerous**, because usually one evaluates E_l increasingly less accurately for increasing l , which can result in an overestimation of the rate of convergence.

Some extrapolations were reported, in which a wrong general analytic form of the asymptotic error was assumed. It is, in this context, at least helpful to know that the truncation error goes as $(L + 1)^{-3}$. *Educated numerical extrapolations* are starting to play an important role in practical calculations striving at high accuracy [41].

The principle quantum number expansion

Although the asymptotic behavior of the partial wave expansion is well understood, an extrapolation based on the E_l is difficult, because for increasing l an increasing size of the basis is needed (unless one uses expansions in $r_>$ and $r_<$ [28], which is only feasible for atoms), so good E_l values for moderately large l are quite expensive.

An interesting alternative is the *principal quantum number expansion* [42]. There is striking evidence (although an analytic proof is still missing) that the error of truncating, say, a CI expansion of the He ground state, after a certain *principle quantum number* n , i.e. after 2s,2p, or 3s,3p,3d etc. goes (like the error of the l -expansion) as $(n_{max} + 1)^{-3}$. The evaluation of the *principle quantum number increments* E_n is much easier than that of the partial wave increments E_l .

Hund's rules

Hund found his rules in 1925 from an analysis of atomic spectra [43, 44]. He stated four rules which determine the **ground state** of an atom.

1. Among the many-electron states arising from the ground configuration the **ground state** has the **largest total spin**.

2. Among the states of the ground configuration with the same largest total spin the **ground state** is the one with the **highest angular momentum quantum number L** .

3a. If the shell is less than half-full, then the ground state has the smallest value of $J = |L + S|$.

3b. If the shell is more than half-full, then the ground state has the largest value of $J = |L + S|$.

These rules have **never been derived from quantum mechanics**, and they have, in spite of their popularity, only a **limited validity**, unless one restricts them to **ground states**.

Rather well justified is, what one may call the **minimal Hund's rule**:

If for an electronic configuration (e.g. $1s2p$) there is only a singlet and a triplet term (e.g. 1P and 3P), the triplet has the lower energy. Generalizable to molecules.

Take an excited $(1s)(nl)$ configuration of the He atom and assume the $1s$ and nl orbitals normalized and orthogonal to each other, the **spinfree wave functions** of the **singlet and triplet** wave functions in the absence of the electron interaction are

$$\psi_{\pm} = 2^{-1/2} \left\{ (1s)(nl) \pm (nl)(1s) \right\}$$

with the $+$ sign referring to the singlet and the $-$ sign to the triplet.

The 0^{th} order energy (treating the electron interaction as a perturbation) is the same for the two states

$$E_{\pm}^{(0)} = \langle (1s)|h|(1s) \rangle + \langle (nl)|h|(nl) \rangle$$

while the 1^{st} order energy contains a **common Coulomb term**, and an **exchange term which enters with opposite sign**.

$$E_{\pm}^{(1)} = \langle (1s)(nl)|V_{12}|(1s)(nl) \rangle \pm \langle (1s)(nl)|V_{12}|(nl)(1s) \rangle$$

The difference between the two states is

$$\Delta E = E_+ - E_- = 2 \langle (1s)(nl)|V_{12}|(nl)(1s) \rangle + \text{higher order terms}$$

One can show that the **exchange integral is always positive** [45]. Assuming that higher-order terms are negligible, one has proven that the triplet state is lower in energy than the singlet state.

Some simple examples.

1s 2s : 1S , 3S controlled by minimal rule, in agreement with first rule.
 3S lowest.

1s 2p : 1P , 3P similar, 3P lowest.

2p² : 3P , 1D , 1S . In agreement with 2nd rule 3P lowest. Why? Not due to exchange. $^1D < ^1S$ in agreement with 2nd rule

2p 3p : 3P , 3D , 3S , 1P , 1D , 1S . Lowest term is 1P , in disagreement with 1st and 2nd rule. Not a ground configuration.

3d² : 3F , 3P , 1D , 1G , 1S . 3F ground term, in agreement with 1st and 2nd rule. Lowest singlet term 1D , not 1G .

The alternating rule for 2-electron atomic states

Russel and Meggers 1927 [46], J. D. M. and W. K. 1993 [11, 12]

Among the two-electron states of the same configuration and the same total angular momentum quantum number L , the triplet is lower in energy than the singlet for natural-parity states while the singlet is lower for unnatural parity states.

The spin-free wave function of an uncorrelated two-particle state with orbital quantum numbers n_1, l_1, n_2, l_2 and total quantum numbers L, M, S is

$$\begin{aligned} \Phi = \Phi_{LMn_1l_1n_2l_2}^S(\vec{r}_1, \vec{r}_2) &= [2(1 + \delta_{n_1n_2}\delta_{l_1l_2})]^{-1/2} \times \\ &\left\{ R_1(r_1)R_2(r_2)\Omega_{LMl_1l_2}(\omega_1, \omega_2) \right. \\ &\left. + (-1)^{S+L+l_1+l_2} R_2(r_1)R_1(r_2)\Omega_{LMl_2l_1}(\omega_1, \omega_2) \right\} \end{aligned} \quad (44)$$

R_1 and R_2 are one-electron functions, depending on n_1, l_1 and n_2, l_2 respectively, while the Ω are angular functions, with ω_k symbolizing ϑ_k and φ_k . Explicitly the Ω are given by

$$\Omega_{LMl_1l_2}(\omega_1, \omega_2) = \sum_{m_1, m_2} (-1)^{l_1 - l_2 + M} (2L + 1)^{1/2} \times$$

$$\begin{pmatrix} l_1 & l_2 & L \\ m_1 & m_2 & -M \end{pmatrix} Y_{l_1}^{m_1}(\omega_1) Y_{l_2}^{m_2}(\omega_2) \quad (45)$$

with Y spherical harmonics and (...) Wigner $3j$ symbols.

Consider two states that agree in all quantum numbers except S , with the radial functions R_1 and R_2 identical in both states. Energy splitting:

$$\begin{aligned} \Delta E = & (1 + \delta_{n_2 n_2} \delta_{l_1 l_2})^{-1} (-1)^{S+L+l_1+l_2} \int dr_1 dr_2 r_1^2 r_2^2 \times \\ & \int d\omega_1 d\omega_2 R_1^*(1) R_2^*(2) R_2(1) R_1(2) r_{12}^{-1} \times \\ & \Omega_{LMl_1 l_2}(\omega_1, \omega_2) \Omega_{LMl_2 l_1}(\omega_1, \omega_2) \end{aligned} \quad (46)$$

The factor $(-1)^{S+L+l_1+l_2}$ is $+1$ for natural parity singlets or unnatural parity triplets and -1 for unnatural parity singlet or natural parity triplets.

In order to prove the alternating rule it is hence sufficient to show that the **integral which multiplies this factor is always positive**. Insert the Laplace expansion of r_{12}^{-1}

$$r_{12}^{-1} = \sum_{n=1}^{\infty} (r_{<}^n / r_{>}^{n+1}) P_n(\cos\vartheta) \quad (47)$$

such that (46) becomes a sum over n terms with either sign.

$$\Delta E = (1 + \delta_{n_1, n_2} \delta_{l_1, l_2})^{-1} (-1)^{S+L+l_1+l_2} \sum_{n=0}^{\infty} G^{(n)} \times$$

$$(-1)^{l+l_1+l_2} \times (2l_1 + 1)(2l_2 + 1) \left\{ \begin{matrix} l_1 & l_2 & L \\ l_1 & l_2 & n \end{matrix} \right\} \left(\begin{matrix} L_1 & l_2 & n \\ 0 & 0 & 0 \end{matrix} \right)^2 \quad (48)$$

where the $G^{(n)}$ are radial exchange integrals

$$G^{(n)} = \int dr_1 dr_2 r_1^2 r_2^2 R_1^*(1) R_2^*(2) R_2(1) R_1(2) r_{<}^n r_{>}^{-n-1} \quad (49)$$

and $\{\dots\}$ is a Wigner $6j$ symbol. In view of the triangular inequalities for the Wigner symbols the sum (48) is finite.

Using a proof of Racah [47] that the radial integrals $G^{(n)}$ are all positive and the **sequence $G^{(n)}/(2n + 1)$ is monotonically decreasing**, further a less well-known **sum rule** involving products of $3j$ and $6j$ symbols [48]

$$\sum_{n=0}^{\infty} (2n + 1) \begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & n \end{Bmatrix} \begin{pmatrix} l_1 & l_2 & n \\ 0 & 0 & 0 \end{pmatrix}^2 = \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 \quad (50)$$

and finally the **observation that the partial sums**

$$\sum_{k=n_{min}}^n (2k + 1) \begin{Bmatrix} l_1 & l_2 & L \\ l_1 & l_2 & k \end{Bmatrix} \begin{pmatrix} l_1 & l_2 & k \\ 0 & 0 & 0 \end{pmatrix}^2 ; n \leq n \leq n_{max} - 1 \quad (51)$$

are positive for natural parity states and negative for unnatural parity states, we were able to **prove the alternating rule**.

The proof just mentioned is of **first-order type**, assuming that the two states with the same n_1, l_1, n_2, l_2 , and L , but different S have the same radial factors R_1 and R_2 . The proof **can be extended** to the case that R_1 and R_2 differ for the two states, e.g. that they are optimized in a Hartree-Fock sense for the states independently. Then we choose for the pair of the states the R_1 and R_2 of the singlet state in case of natural parity, and of the triplet in case of unnatural parity. For the other state we then get an upper bound to its exact Hartree-Fock energy, i.e. the **energy difference between the two states, which is positive in either case, is a lower bound** to the *exact* difference between the Hartree-Fock states, which is hence positive as well.

We have considered here **genuine two-electron states**, but the proof is easily generalized to the example of **two electrons in open shells outside an arbitrary number of filled closed shells**.

One sees from (44) that for $n_1 = n_2$ and $l_1 = l_2$, which implies $R_1 = R_2$, the two contributions in (44) agree, except for the sign factor, such that only $S + L + l_1 + l_2 = \text{even}$ leads to a non-vanishing wave function, i.e. only **natural-parity singlets and unnatural parity triplets** are possible. The wave function becomes

$$\Phi = R(r_1)R(r_2)\Omega_{LMll}(\omega_1, \omega_2) \quad (52)$$

and the electron interaction contribution to the energy is

$$E_I = (-1)^L \sum_{n=0}^{\infty} F^{(n)} (2l + 1)^2 \left\{ \begin{matrix} l & l & L \\ l & l & n \end{matrix} \right\} \left(\begin{matrix} l & l & n \\ 0 & 0 & 0 \end{matrix} \right)^2 \quad (53)$$

with

$$F^{(n)} = \int dr_1 dr_2 r_1^2 r_2^2 |R(1)|^2 |R(2)|^2 r_{<}^n r_{>}^{-n-1} \quad (54)$$

Only $n = 0, 2, \dots, 2l$ is possible. The term with $n = 0$ in the sum (53) is independent of L .

Improved Hund's rules for 2-electron atoms

The **alternating rule** is an extension of the minimal rule. It does not tell us, why for a $2p^2$ configuration the ground term is 3P . This is **not due to exchange**.

We need three more rules

(a) The **unnatural parity rule**: Among the **averages** of singlet and triplet terms of a configuration the lowest is that of an **unnatural parity state**.

(b) The **maximum- L rule**: Among the averages of singlet and triplet **unnatural parity states** for each L , that with the **largest L is lowest**.

A similar rule does not hold for natural parity states. Already for the d^2 configuration one finds $^1D < ^1G < ^1S$. [45].

(c) The singlet-triplet splitting rule: **The singlet-triplet splitting of the unnatural parity states with optimum L** is not so much smaller than that of any other states, such that the lowest state of the latter could become the lowest state of the configuration.

We consider an $(nl)(n'l')$ configuration. There are states with $L = |l - l'|, |l - l'| + 1, \dots, l + l'$. Let

$$l_1 = \min(l, l'); \quad l_2 = \max(l, l') \quad (55)$$

The average energy of the singlet state and the triplet state for a given L is expressible in terms of $l_1 + 1$ Slater-Condon parameters F^k , with

$$k = 0, 2, \dots, 2l_1, \quad (56)$$

while the singlet-triplet splitting requires the same number of G^k parameters with

$$k = l_2 - l_1, l_2 - l_1 + 2, \dots, l_2 + l_1. \quad (57)$$

Energy in the framework of the Slater-Condon-Racah-Wigner theory

$$E(L, S) = E_0 + \sum_{k=0}^{2l_1} a_k F^k + (-1)^S \sum_{k|l_2-l_1|}^{l_2+l_1} b_k G^k, \quad (58)$$

$$a_k = (-1)^L \begin{pmatrix} l_1 & l_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2 & k \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l_1 & l_2 & L \\ & l_1 & k \end{matrix} \right\} (2l_1 + 1)(2l_2 + 1) \quad (59)$$

$$b_k = (-1)^{l_1+l_2+L} \begin{pmatrix} l_1 & l_2 & k \\ 0 & 0 & 0 \end{pmatrix}^2 \left\{ \begin{matrix} l_1 & l_2 & L \\ & l_1 & k \end{matrix} \right\} (2l_1 + 1)(2l_2 + 1) \quad (60)$$

E_0 is common to all terms and contains the one-electron part. Use the sum rule (50) as well as a related one:

$$\begin{aligned} & (-1)^L \sum_k (2k + 1) \begin{pmatrix} l_1 & l_1 & k \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_2 & l_2 & k \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l_1 & l_2 & L \\ & l_1 & k \end{matrix} \right\} \\ & = \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 (-1)^{l_1+l_2+L}, \end{aligned} \quad (61)$$

This implies

$$\sum_k (2k + 1)a_k = (2l_1 + 1)^{-1}(2l_2 + 1)^{-1} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2, \quad (62)$$

Both sums (50) and (61) vanish for unnatural parity states and are positive for natural parity states. This allows us to eliminate one term in the sum (58) for the unnatural parity states. We find it convenient to define

$$\tilde{F}^k = F^k - \frac{2k + 1}{4l_1 + 1} F^{2l_1}, \quad (63)$$

so that

$$E_{ST}(L) = \frac{1}{2}[E(L, 0) + E(L, 1)] = E_0 + \sum_{k=0}^{2l_1-2} a_k \tilde{F}^k + \tilde{a}_{2l_1} F^{2l_1}, \quad (64)$$

$\tilde{a}_{2l_1} = 0$ for unnatural parity states

$$\tilde{a}_{2l_1} = (2l_1 + 1)^{-1}(2l_2 + 1)^{-1} \begin{pmatrix} l_1 & l_2 & L \\ 0 & 0 & 0 \end{pmatrix}^2 (4l_1 + 1)^{-1} > 0$$

for natural parity states.

The sum rule (62) is a direct reflection of the angular symmetry hole for unnatural parity states in the one-configuration approximation, *i.e.*, of the fact that for these states Φ vanishes for $\omega_1 = \omega_2$.

Note that $a_0 = 1$ (independent of l_1, l_2, L) and that for unnatural parity states there are only $l_1 - 1$ nontrivial terms, namely those with

$$k = 2, 4, \dots, 2l_1 - 2 . \quad (4.8)$$

Since the F^k are positive and form a monotonically decreasing sequence, this also holds for the \tilde{F}^k .

The energy expression depends on the numerical values of all F_k and G_k , for the singlet-triplet average on the F_k .

There are sum rules, in view of which not all F_k enter.

Example $l_1 = l_2 = 1$ e.g. 2p3p.

$$E_{ST}(L) = E_0 + \tilde{a}_2(L)\tilde{F}_2; \quad \tilde{F}_2 > 0$$

$$\tilde{a}_2(L) = 0 \text{ for unnatural parity (P)}$$

$$\tilde{a}_2(L) > 0 \text{ for natural parity (S, D)}$$

The P-pair (with unnatural parity) is lowest.

Example $l_1 = l_2 = 2$ e.g. 3d4d.

$$E_{ST}(L) = E_0 + \tilde{a}_2(L)\tilde{F}_2 + \tilde{a}_4(L)\tilde{F}_4; \quad \tilde{F}_2 > 0, \quad \tilde{F}_4 > 0$$

$$\tilde{a}_4(L) = 0 \text{ for unnatural parity (P, F)}$$

$$\tilde{a}_4(L) > 0 \text{ for natural parity (S, D, G)}$$

With reasonable assumptions on the ratio between F_2 and F_4 one finds that the unnatural parity states (P, F) are lower, and that among these the F-pair is lowest. The splitting according to the alternating rule is small enough, not to affect this result.

Example $l_1 = l_2 = 3$ e.g. $4f^2$.

Only slightly more complicated. Both the unnatural parity rule and the maximum L rule hold. The ground term is 3H (L=5).

Example $l_1 = l_2 = 4$ e.g. $5g^2$.

Now depending on the values of the Slater-Condon parameters, the states 3H (L=5) and 3J (L=7) become competitive.

Example $l_1 = l_2 = 5$ e.g. $6h^2$.

The ground term is **still of unnatural parity**, and hence a triplet, but it belongs to L=7 rather than L=9. **The maximal L-rule no longer holds.**

A qualitative explanation of the results appears difficult.

The (most generally valid) **alternating rule** tells us that **short range radial correlation** (exchange) lowers the energy. This favors the **triplet for natural parity**, and the **singlet for unnatural parity**.

Short-range angular correlation is at the origin of the **unnatural-parity rule**. This favors **unnatural parity over natural parity** states.

The maximum-L rule is related to **long-range angular correlation**. This favors the maximum L only for l_1 and l_2 not too large. The best L is actually $l_1\sqrt{2}$

Table 3: Estimates of the optimum L for unnatural parity states

l_1	1	2	3	4	5	10	20
1 term i.e. $\sqrt{2} l_1$	1.414	2.828	4.243	5.657	7.071	14.142	28.284
2 terms	1.621	3.036	4.450	5.864	7.278	14.349	28.491
exact	1.436	2.928	4.373	5.804	7.230	14.323	28.478
$2l_2 - 1$	1	3	5	7	9	19	39

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