Università degli Studi di Perugia
Facoltà di Scienze Matematiche Fisiche e Natural

Hydrogenoid orbitals revisited: from Slater orbitals to

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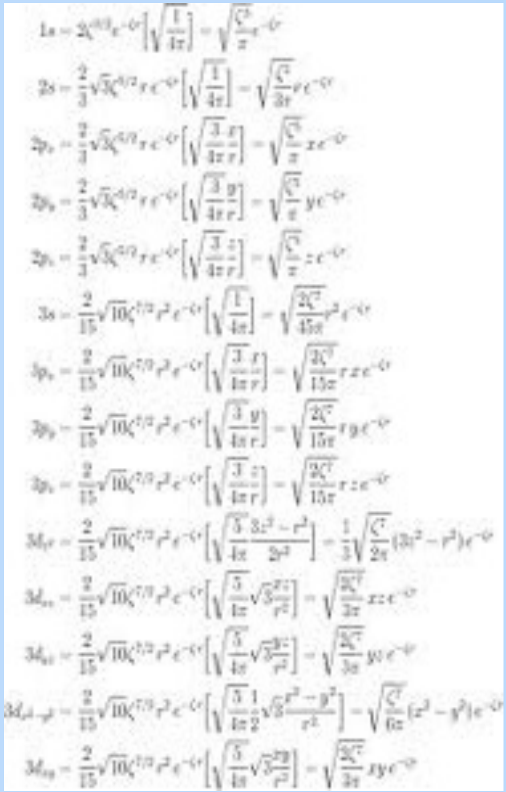
Structure:

- Slater Orbitals: origins and features
- Coulomb Sturmian as basis set
- Coulomb Sturmians in momentum space
- Relationship between Coulomb Sturmians and Slater orbitals
- Evaluation of computing costs of many body integrals using Coulomb

Slater Orbitals: origins and features

$$\chi_{nlm}^{\zeta} = N_n^{\zeta} r^{n-1} e^{-\zeta r} Y_{lm}(r)$$



In 1930, J.C. Slater created a new class of orbitals to simplify the calculation of atomic features (ion radius, ionization energies….) introducing a parameter to approximate the experimental data in relationship with the electronic screening of the nuclear charge.

These orbitals do not reproduce the zero points of the wave funciton: ζ is the parameter, depending on the screening constant.

Slater orbitals however can approximate the real wave function close to and far from the nuclei; also, the hydrogenoid orbitals can be written like a linear combination of Slater orbitals.

Coulomb Sturmians as basis sets

If we want to completely describe a chemical system with accuracy, we need to use a complete and orthonormal basis set.

$$\Psi = \sum_p c_p \varphi_p.$$

Coulomb Sturmian orbitals can be used as a complete basis set without adding the continuum states, as needed in the case of hydrogenoid orbitals. So, they can be implemented on structure or dynamics calculations.

$$(\hat{T} + E_0)\psi = \frac{\alpha_{nl}}{r}\psi$$

Coulomb Sturmians are so close to the real wave function that just a few of them are enough to quickly converge to the real value.

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$$(\hat{T} + E_0)\psi = \frac{\alpha_{nl}}{r}\psi$$

$$\psi_{nlm}(r) = N_{nl}(2p_0 r)^l e^{-p_0 r} F(l+1-n \mid 2l+2 \mid 2p_0 r) Y_{ml}(r)$$

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Coulomb Sturmians in momentum space

Using the Fourier Trasform and the Fock's projection we can demostrate that, in momentum space, Coulomb Sturmian orbitals are isomorphic to O(4) hyperspherical harmonics. Therefore it is possible to rewrite Sturmian orbitals as hyperspherical harmonics $Y_{n-1,l,m}$

$$\psi_{nlm}(p) = (-1)^{n-1-|m|}(i)^{l+m+|m|}\frac{4p_0^{\frac{5}{2}}}{(p_0^2+p^2)^2}Y_{n-1,l,m}(\chi,\vartheta,\varphi)$$

Moreover, the tree method allows us to avoid the perturbative method in the cases where the right sistem of coordinates can be used to simplify the calculation (Ex.: a strong external elettric field). The operation on hyperspherical harmonics can be seen as an operation of hyperangular momenta, so it justifies the notation in 3j, 6j symbols.

Relationship between Coulomb Sturmians and Slater orbitals

Coulomb Sturmian orbitals have many benefits but, at the same time, are a real challenge for the implementation of algorithms.
We want to determin the exact connection between Coulomb Strumian orbitals and the Slater ones, so we can use the completeness of Sturmians combined with new computational methods built up for Slater orbitals.

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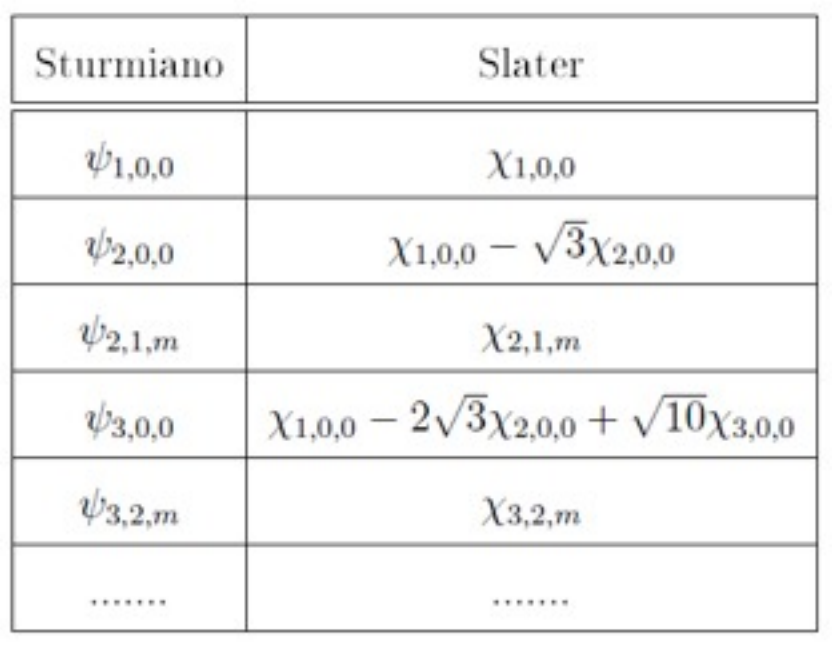

Sturmiano	Slater
$\psi_{1,0,0}$	$\chi_{1,0,0}$
$\psi_{2,0,0}$	$\chi_{1,0,0} - \sqrt{3}\chi_{2,0,0}$
$\psi_{2,1,m}$	$\chi_{2,1,m}$
$\psi_{3,0,0}$	$\chi_{1,0,0} - 2\sqrt{3}\chi_{2,0,0} + \sqrt{10}\chi_{3,0,0}$
$\psi_{3,2,m}$	$\chi_{3,2,m}$
....	....

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$$L_n^a(x) = \sum_{i=0}^{n} (-1)^i \binom{n+a}{n-i} \frac{x^i}{i!}$$

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$$\psi_{nlm}(r) = \sum_{k=0}^{n-l-1} \frac{N_{nl}^{p_0}}{N_\nu^{\zeta}}\frac{(-1)}{k!}\binom{n+l}{n-l-1-k}\chi_{\nu ml}(\beta r)$$

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$$\psi_{nlm}(r) = \sum_{k=0}^{n-l-1} \frac{N_{nl}^{p_0}}{N_{\nu}^{\zeta}} \frac{(n+l)!}{(n-l-1)!(2l+1)!} \frac{(-n+l+1)_k}{(2l+2)_k} \frac{\tilde{\chi}_{\nu lm}(\beta r)}{k!}$$

$$\nu = k + l - 1$$

$$k = \nu - l + 1$$

Many body Integrals

$$\left[-\frac{1}{2}\sum_{i=1}^{N}\nabla_i^2-\sum_{a=1}^{M}\sum_{i=1}^{N}\frac{Z_a}{|r_i-R_a|}+\sum_{i>j}\frac{1}{|r_i-r_j|}+\frac{p_0^2}{2}\right]\Psi(\xi)=0$$

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$$\Phi_{\nu,m}(x)=\frac{1}{\sqrt{N!}}$$

$$\begin{vmatrix}
\psi_{n_1l_1m_1m_{s1}}(x_1^m) & \psi_{n_2l_2m_2m_{s2}}(x_1^m) & \cdots & \psi_{n_Nl_Nm_Nm_{sN}}(x_1^m) \\
\psi_{n_1l_1m_1m_{s1}}(x_2^m) & \psi_{n_2l_2m_2m_{s2}}(x_2^m) & \cdots & \psi_{n_Nl_Nm_Nm_{sN}}(x_2^m) \\
\vdots & \vdots & \ddots & \vdots \\
\psi_{n_1l_1m_1m_{s1}}(x_N^m) & \psi_{n_2l_2m_2m_{s2}}(x_N^m) & \cdots & \psi_{n_Nl_Nm_Nm_{sN}}(x_N^m)
\end{vmatrix}$$

$$x_n^m = |x_n - X_m|$$

Many body Integrals

$$S_{nlm}^{n'l'm'}(R) = \frac{n}{p_0}\int \psi_{nlm}(x)\frac{1}{|x|}\psi_{n'l'm'}(x-R)dx$$

Shibuya and Wulfman method for the formulation of molecular orbitals involves the calculation of many body integrals.

The convergence rate of the algorithms represents the highest limit to the large application of this method.

Conclusions

Coulomb Sturmian orbitals can be read as hyperspherical harmonics in the momentum space. This property can simplify the calculation of non-standard systems, like atom into an external elettric field or excitated states.

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The relationship between Coulomb Sturmians and Slater orbitals can be used to improve the calculation rate of this method, recovering all the extensive work on Slater orbitals in the application of Sturmian basis sets.

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The search of analytical solutions of many body integrals in the momentum space is the real challenge for the application of this method for dynamics and structure calculations.