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Partial Derivation of the Sqrt(N) Member in Resonant-Consistent Method

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Abstract

In the section „Theoretical derivation and explanation of method” of the article „Optimization of basis sets by a resonant-consistent method for elements and basic compounds” [1]. The following equation was introduced and partially derived:

$$Z_{effrel}/Z = x_0/x_{rel} = \left(\sqrt{E/(E_R \cdot \sqrt{N})} \right) / \sqrt{1 - (Z(e^2/(2\epsilon_0 hc))/n)^2} \Big)^a \cdot Z_{effrelprev}/Z^{(1-a)} \quad (1)$$

for optimizing the exponents of Slater basis in electron systems. The remaining problem involves a term $\sqrt{N}$ related to the interaction with other electronic kinetic energies, which is not yet fully explained. This article explains key aspects of this term and shows how the algorithm works.

The Edge Cases of Application the Resonant-Consistent Equation System with Two Nucleuses

In a system with one electron and two nuclei, it is not necessary to include the second or additional nuclei in the Z term of Equation (1), nor is it required for computing the initial Rydberg energy. When the distance to the other nuclei approaches infinity, their electrostatic nuclear force tends toward zero, leaving the system unaffected by them.

Conversely, when the distance to another nucleus approaches zero, the resonance-consistent algorithm converges by multiplying the wavefunction distance by Z/Z_{all} , where Z_{all} is the sum of all protons in all nuclei, and Z is the number of protons in the specific nucleus where the electron oscillates in Equation (1). The following relations apply:

$$E = E_R/(Z/Z_{all})^2, x/x_0 = (Z/Z_{all}), V = V_R/(Z/Z_{all})^2, T = T_1/(Z/Z_{all})^2 \quad (2)$$

These are derived from the dependencies of the wavefunction's kinetic energy T and potential energy V on Z and the length x from the equations in the article “Optimization of basis sets by a resonant-consistent method for elements and basic compounds” [1]. This equality ensures that it is not necessary to include secondary nuclei in Equation (1), as the dependency of their energy levels on the wavefunction length is non-linear.

Also, electrostatic, electrodynamic, and correlation forces from electrons in other nuclei can be treated only by including their contributions to the energy levels, and it is not necessary to change the constants $\sqrt{N}$.

This is because these electrostatic forces (electron repulsion integrals) of these terms have directional and non-directional parts. The directional parts do not influence the state of the wavefunction beyond their influence on the energy levels in the sense of equation (1), as is the case with the other nuclei mentioned above. The non-directional parts are entirely eliminated by the resonance integral (or in the antibonding state, where no overlap is present). This can be described by equation:

$$K_{ij}=V_{ij} \cdot S_{ij} \quad (3)$$

Furthermore, there are inter-electron kinetic integrals of electrons in other nuclei with no influence on the state of the wavefunction of the investigated electron beyond their influence on the energy levels in the sense of equation (1). This is because the influence of the non-directional part of the electrostatic forces is entirely eliminated by the resonance integral, and there is no bonding between them and the inter-electron kinetic integrals. This is why this equation for H_2 exact.

System with One Nucleus and Two Electrons

In a two-electron system with one nucleus, the inter-electron kinetic integrals are tied to electrostatic forces. This occurs because resonance integrals are not used in their description, and electron-electron repulsion integrals have a purely non-directional character.

For example, in a Helium (He) atom with two electrons sharing the same wavefunction, the inter-electron kinetic energy has the same magnitude as the intra-electron wavefunction kinetic energy. Thus, the kinetic integral from the wavefunction appears twice in the electron's energy level. Its estimated new wavefunction length must be scaled by a factor of $\sqrt{(N)}$ because the inter-electron kinetic energy integral is negative. (A positive sign can only occur in the case of a violation of the Pauli exclusion principle). In the overall system energy, the one-electron kinetic integral appears once instead of twice, meaning one one-electron kinetic integral is canceled.

In a one-electron system, the equilibrium state of the wavefunction is given by the global minimum of the sum of the nuclear and kinetic integrals, which is described by the Rydberg equation. The one-electron kinetic integral is positive and scales with the inverse second power of the average wavefunction length. The nuclear attraction integral is negative and decreases with the first power of the average wavefunction length.

Because the inter-electron kinetic integral decreases with the first power of the length of the first wavefunction and the first power of the average length of the second wavefunction, we can make an assumption. The derivative of the kinetic energy with respect to length is one-half of the derivative for the one-electron integral. Consequently, the equilibrium wavefunction lengths fall by a factor of one-half, and the energy level is decreased by a factor of two.

If we update only the kinetic integral parts, we obtain a $\sqrt{(N)}$ -times rise in system energy and a $\sqrt{(N)}$ -times shortening of the wavefunction length.

However, if we use equation (1), we apply the dependency $x \sim 1/\sqrt{(E)}$ just as we do for the kinetic energy integrals. This equation is used for iteratively solving the wavefunction lengths, and thus we must use the estimated one-centered kinetic energies for update the lengths and then recompute the potential energies and inter-electron kinetic energies and other members. This algorithm lead in He atoms to the true Hamiltonian, energy levels and wavefunctions. This algorithm can be thus generalized too for atomic shells with wavefunctions with the same Z_{eff} .

System with One Nucleus and Two Electrons in Different Wavefunctions

In a system where two electrons occupy different wavefunctions, we use an orthogonal basis with different principal quantum numbers (for example, 1s and 2s, or 1s and 2p wavefunctions).

The inter-electron kinetic energy integrals are equal to 2× smaller (due to an 8× lower overlap, 2× smaller distances in 1s wavefunctions, and a 2× steeper wavefunction derivative in the inner region) than between 1s and 1s electrons. However, the second shell can hold up to 4× more electrons when $n = 2$ is full.

This enables 2× more secondary effects. These secondary effects also appear in open-shell systems, which feature high correlation energies due to a low energy barrier to excitation. Because with the count of electron is for every main quantum number n function of its second power, this can be generalized for relations of electrons with all main quantum number in orthonormal electron system.

The equilibrium of a system with two electrons is empirically orthonormal. This is further evidence that kinetic integrals from other atoms may not be involved in the $\sqrt{(N)}$ component.

Practical use in Small Molecules and Atoms with $Z \leq 30$

Because of these facts, the resonant-consistent method is also usable for multi-electron systems with more than one shell. However, it requires very careful treatment of correlation energies and a high-resolution grid, as multi-layer implementations introduce computational instability.

For molecular computations, it is also necessary to treat the electron density shift between atoms and its influence on the $\sqrt{(N)}$ factor using ab-initio methods.

This method can handle non-orthonormality (and eliminate it) by bringing energy levels closer together when there is little or no pressure for non-orthonormality (e.g., shielding between shells, external fields, relativistic effects). This works because poorly estimated energy levels are updated faster than more accurate ones.

Practical use in Relativistic Conditions with Relativistic-Reshaped STOs

Under relativistic conditions, ordinary Slater-type orbitals (STOs) become inadequate due to relativistic deformations. The Dirac equation

$$(i\gamma^\mu \delta_\mu^{-m})\psi = 0, \quad (4)$$

where γ^μ are gamma matrices, δ_μ are derivations over space and time and ψ is the wavefunction was firstly introduced in [2]. This equation is solved iteratively using various methods (such as the Douglas–Kroll–Hess and ZORA approaches). Crucially, the relativistic reshaping of Slater-type orbitals is constrained by the condition of equal kinetic energies for each radial node.

When this condition is maintained, the radial node structures for the 1s, 2s, and higher s-orbitals are accurately reproduced. As relativistic effects increase, the radial nodes contract and experience heightened spatial overlap. Specifically, the nodal structure of the 2s orbital (excluding its outermost node) tends to overlap with the node of the 1s orbital. This behavior generalizes to any s-orbital with principal quantum number n relative to the $n-1$ s-orbital of the atom. Similarly, for orbitals with an azimuthal quantum number $l > 0$ (p, d, f, etc. orbitals), higher-order nodes of $l + 1$ classification are the first to overlap. Finally, the inter-electron kinetic integrals tend to scale as a function of $1/n^2$.

The origin of this effect lies in the relativistic speed limit of light, which increases the effective mass of the electrons. Consequently, there is a higher probability of finding these electrons closer to the nucleus. Because they spend more time in this region, the first radial node of the wavefunction becomes more deformed and shifted toward the nucleus than the other radial nodes. This shift is dictated by the requirement that the kinetic energy terms of each wavefunction's radial node remain equal.

Due to the condition of equal kinetic energy terms at each radial node of the wavefunction, this second condition drives the kinetic integrals between the 1s and other s-orbitals toward ratios of $1/n^2$ as n increases. This—combined with secondary effects on orbitals with the same principal quantum number n but different azimuthal quantum numbers l , as well as the $2n^2$ occupancy of each n -shell—ensures that the net bonding network within the electronic structure is maintained mainly via s-electrons. Meanwhile, the p, d, f, and higher orbitals overlap at higher nodes, causing a uniformity of the bonding effect in higher shells.

Thus, equation (1) remains relevant under relativistic conditions when using correct relativistic basis functions, despite their non-orthonormality. In practical applications involving two or more atoms, ab initio methods must be used to express the occupation of higher orbitals. This occupation is driven by positive kinetic integrals sharing the same set of quantum numbers (as bringing the nuclei closer together makes the occupation of higher orbitals energetically favorable due to the Pauli exclusion principle). The constant $\sqrt{\langle(N)\rangle}$, which expresses the bond between the local energy level minimum and the system's Hamiltonian minimum, is maintained separately for the localized atoms due to resonance integrals, as previously demonstrated using the example of H_2 molecule.

The practical computational accuracy is limited by the square of the ratio of the orthonormalized to non-orthonormalized Hamiltonian operators, as well as by spin-orbit coupling effects and the energy levels in the valence shells. For precise spectral simulations of open-shell systems, the spectra must be fine-tuned using a gradient-descent method.

This analysis shows that the accuracy of the resonant-consistent method is limited by:

- The non-orthonormality of the basis set in the source atoms. These differences can be investigated using the second power of the ratio of the orthonormalized to non-orthonormalized Hamiltonian, and they become critical under relativistic conditions.
- Overlaps with non-bonding electron wavefunctions, which represent another form of non-orthonormality. These overlaps can be reduced using the Roothaan–Hall procedure because they are not energetically beneficial. Furthermore, the true correlation energy and kinetic integrals are derived from the self-consistent state of the electron system, which can be back-projected onto the basis.
- Deviations from Slater-type orbitals, which cause the elimination of the nodal structure, thereby reducing the derivatives of the wavefunctions in their inner regions and consequently lowering the inter-electron kinetic integrals.

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