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Optimization of Basis Sets by a Resonant-Consistent Method for Elements and Basic Compounds

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Abstract

This article presents a novel approach for creating optimized basis sets, which are fundamental to quantum chemistry calculations. Basis sets, comprising atomic orbitals, play a crucial role in describing electronic structure, influencing a wide range of computations of physicochemical properties. The article reviews the historical context, theoretical foundations, and current developments in basis sets, followed by the introduction of a new basis set computed using a new variant of self-consistent field method - resonant-consistent method for atoms, ions, and simple molecules. The proposed algorithm offers a partial solution to the optimization of basis (atomic orbitals) parameters, which can be employed prior to final full optimization via a gradient descent method to minimize energy according to the basis (atomic orbitals). This approach is noteworthy for its potential to conserve computational resources and address issues related to local minima in energy landscapes. In comparison to other self-consistent methods that iteratively update the effective nuclear charge, this method has versions without empirical parameters.

Keywords: Slater Type Orbital, Basis Set Optimization, Self-Consistent Field Method, Wavefunction Theory, Quantum Oscillator Based Approach

Introduction

The accuracy of molecular property predictions in quantum chemistry heavily relies on the quality of the basis sets employed in electronic structure computations. Basis sets, comprising atomic orbitals, serve as a set of wavefunctions used to expand into molecular orbitals, enabling the efficient representation of electronic wavefunctions. The choice of basis set is a critical factor that determines the precision of calculated energies, geometries, and spectroscopic properties. Over the decades, the development and optimization of basis sets have been driven by the need for improved accuracy and efficiency in computations.

The historical evolution of basis sets can be traced back to the early days of quantum chemistry, when minimal basis sets were employed due to computational limitations. Pioneering works by Slater Swirles Pople and others laid the groundwork for the conceptualization of basis sets and introduced mathematical functions to represent atomic orbitals [1-4]. As computational resources expanded, so did the sophistication of basis sets, with the introduction of polarization functions diffuse functions correlation-consistent basis sets by Duning et all. and polarization-consistent basis sets by Jensen [4-8].

Contemporary research in this field focuses not only on expanding the range of chemical systems that basis sets can accurately describe but also on optimizing their performance. Basis set optimization methods aim to strike a balance between achieving high accuracy in electronic structure predictions and minimizing computational cost. These methods involve the systematic refinement of basis set parameters, often through fitting to experimental data and benchmark calculations [6].

The first widely used basis sets were the Slater-type orbitals (STOs), which are derived from electrostatic forces between nuclei and electrons in hydrogen-like atoms and ions. The shapes of these basis sets are derived from the condition of minimizing the overlap integrals between these orbitals [1]. The main quantum number n represents the sum of the counts of half-waves in the radial and angular parts of the basis, the second quantum number l represents the count of

half-waves in the angular part of the basis, the magnetic quantum number m represents the orientation of the basis in space, and the spin quantum number s is the inner rotational moment of the electron, which generates the magnetic field (with no equivalent in classical mechanics).

Next, the STOs were modified using the model of shielding of nuclear charge by other electrons, known as the Slater model of shielding. The Slater model of shielding is an empirical model for improving the precision of the STOs basis and the precision of physical properties calculated from STOs [2]. The effects caused by the theory of relativity, such as spin-orbit coupling and basis contraction, which influence the basis sets, were described by Swirles [3].

In the next step of development basis functions were the STO replaced by the Gaussian basis, which consist of radial part in form of set of Gaussian functions, which are derived from the STOs and angular part, which is the same as in STOs. The advantages of this basis are the good analytical partial solutions of integrals of Gaussian functions for facilitating the quantum-chemistry calculations, flexibility and possibility of using polarization functions and diffuse functions [4,5].

Further developments of basis sets focused on including correlation effects in their development. Correlation-consistent basis sets are optimized using the gradient descent method to minimize correlation energy according to the parameters of primary Gaussians of the basis. The correlation energy is computed using ab initio methods, and the resulting electronic structures and properties are compared with experimental data, with the diffuse and polarization functions iteratively updated to reach energy minima [6].

Recently, polarization-consistent basis sets were developed for use in density functional theory. These basis sets are developed by adjusting the diffuse and polarization functions using the Newton-Raphson method (method of tangents) to find the minima of the polarization parts of the total energy, and then physicochemical properties (dipole moments, etc.) are calculated. The calculation of properties can be performed using density functional theory or the Hartree-Fock method, with the similarity of convergence criteria [7]. Diffuse functions are necessary for density functional theory computations of anions [8].

Today, an open-source program called BasisOpt has been developed for optimizing correlation-consistent and polarization-consistent basis sets in a Python interface. This program allows for the construction of various optimization algorithms for basis sets adjusted to specific chemical species – adaptive basis sets [9]. Computing physical properties with a full basis set is computationally challenging, and consequently, inner electrons can often be replaced by pseudopotentials. For computing pseudopotentials, the open-source program OPIUM (Open-source Pseudopotential Interface/Unification Module) can be used [10].

In this article, a new method for optimizing basis sets (atomic orbitals) is presented, using a resonant-consistent method and the dependence of quantum oscillator effective length on oscillation energy. The energy levels of electrons are iteratively computed from nuclear attraction, Coulombic integrals, exchange integrals, spin-orbit coupling, correlation energies, and other energetic influences, and new shielding coefficients are evaluated to reach convergence – harmony of energy levels with kinetic energies of oscillations of the basis functions.

Methods:

Theoretical Derivation and Explanation of Method

The method is based on the assumption that electrons move in orbitals in an oscillatory-rotational manner. and on the dependence of average lengths of oscillations on energy levels of basis functions, expressed by the equation of the harmonic quantum oscillator:

$$E = \hat{H} = \hat{p}^2/(2m) + \frac{1}{2}m\omega^2\hat{x}^2, \quad (1)$$

where E is energy of the oscillating particle, H is the Hamiltonian operator of the oscillating particle, p is its oprator momentum, m is its mass, ω is the angular speed, and x is operator the coordinate range. From equation (1) we can derive:

$$x \sim \sqrt{(E)}, \quad (2)$$

where x is the average coordinate difference of oscillations between the center and edge, this dependency is right too for other shapes of wavefunctions.

The Slater-type orbitals are harmonic functions, comprising both radial and angular components, and are derived under the condition that the sum of potential and rotational kinetic energy equals the vibrational kinetic energy. The exponent indirectly depends on the effective nuclear charge Z_{eff} of the oscillation center [2].
Thus:

$$x_0 \sim 1/Z \text{ and } x \sim 1/Z_{eff}, \quad (3)$$

where x_e is the average oscillation length with $Z_{eff} = Z$ (real nuclear charge). The energy levels of Slater-type orbitals of single electron-nucleus systems are described by the Rydberg formula:

$$E_R = hcR_\infty Z^2/n^2 \text{ with } R_\infty = (\mu_e e^4)/(8\varepsilon_0^2 h^3 c), \quad (4)$$

where E_R is the energy level from interaction electron-nucleus, h is the Planck constant, c is the speed of light, R_∞ is the Rydberg energy constant, Z is the nuclear charge, n is the main quantum number, μ_e is the reduced electron mass, e is the elementary charge, and ε_θ is the permittivity of vacuum. From equations (2) – (4) we can derive for Z_{eff}:

$$Z_{eff}/Z = x_0/x = \sqrt{(E_R/E)}, \quad (5)$$

where E is the energy level of the Slater basis. For electrons oscillating in an electron system with more electrons, we need to use a normalization constant of the electron system – √(N) to describe deflection of electrons by other electrons on the atom and discriminating the oscillatory behavior:

$$\left(-T_{ii}{}^2 \cdot N\right)/E^2 = 1, -T_{ii} \cdot \sqrt{(N)}/E = 1 \quad (6)$$

$$Z_{eff}/Z = x_0/x = \sqrt{\left(\left(E_R \cdot \sqrt{(N)}\right)/E\right)}. \quad (7)$$

This approximation is precise for He atom with average angle between between first electron-nucleus-second electron 90° without computing the correlation energy [11]. For restricted model of harmonic oscillation with this angle constant to 90° is the average angles for deflective force of electrons are 45°and sin 45° is 1/√2 , which correspond to factor 1/√N and creating a oscillator-rotatory loop with constant angle particle distances and remaining angles. For more oscillating particles are forces projected from more directions and too restrict oscillatory behavior too for electrons in different energy levels by the same magnitude due to changes in angle distributions. Further verifications may be done via Monte Carlo simulation.

We add relativistic corrections from [3] according to the formula in the next step:

$$x_{rel}/x = \sqrt{(1 - (Z\,(e^2/(2\epsilon_0 hc))/n)^2)} \text{ into term} \quad (8)$$

$$Z_{effrel}/Z = x_0/x_{rel} = \sqrt{\left(E/\left(E_R \cdot \sqrt{(N)}\right)\right)}/\sqrt{(1 - (Z\,(e^2/(2\epsilon_0 hc))/n)^2)} \quad (9)$$

where $Z_{eff\ rel}$ is the relativistic corrected effective nuclear charge, and x_{rel} is the relativistic corrected effective length of oscillations. If this equation is solved iteratively, a linear combination of new and old iterations is used, like a recurrent neural network:

$$Z_{effrel}/Z = x_0/x_{rel} = \left(\sqrt{\left(E/\left(E_R \cdot \sqrt{(N)}\right)\right)}/\sqrt{(1 - (Z\,(e^2/(2\epsilon_0 hc))/n)^2)}\right)^a \cdot Z_{effrelprev}/Z^{(1-a)}, \quad (10)$$

where $Z_{eff\ rel\ prev}$ is the old $Z_{eff\ rel}$ and a is the coefficient of linear combination of a new and old iteration.

He Correlation Energy

It was discovered for two-electron systems like Helium by Kestner et al. that the correlation effects cause anharmonicity in the angular part of the wavefunction, and when one electron is in a specific point of space, the second particle is not able to be in specified distances from the first electron, which causes lowering probabilities of its presence in low angles in the system first electron - nucleus - second electron, and its angular part of the wavefunction can be described by restricting this angle to the first particle [11]. A computed value of Helium correlation energy is around 1.1 eV.

In the practical implementation of the resonant-consistent algorithm, coulombic integrals with lowered values were used, which were computed from increased effective distances between electrons -(2+2*ϕ))/3·r_1, where Phi is the golden ratio, and r_1 is the effective distance of electrons to the nucleus, and with this shape, the iteration algorithm converges to the true value of Helium total energy.

Other Variants of a Correlation Energy Expression

The proposed optimization algorithm requires the right values of correlation energy backward calculated for specific basis. Using the analytical shape of Helium correlation energy gives good results in specific cases and in other cases may serve only as a quick preliminary step for next optimization. The correlation energy can be expressed by density functional theory, for example, by the PBE density functional random phase approximation (RPA), or by higher ab-initio methods (Moller-Plesett perturbation theory, coupled cluster method, configuration interaction method) [12].

For systems with chemical bonding, the effects of electron localization via Roothaan equations - a Hartree-Fock method

or other basis mixing algorithm - must be back-computed to the basis. In these methods the energy levels of the resulting orbitals must be recomputed to the basis using the Slater determinant (table of basis linear combination coefficients of basis to orbitals). For this optimizing step is recommended a RPA approximation.

Strengths and Weaknesses of Algorithm

The proposed algorithm has theoretically lower computational resources consumption in comparison with gradient-descent optimization of basis, which requires computing the gradients, but is not able to optimize the shape of orbitals to the right shape.

The Slater type orbtals were derived for condition of equality of sum potential and rotational energy and the proposed algorithm is usable for Slater type orbitals, polarized Slater type orbitals or its combinations. For optimizing the basis sets of single atoms, a tandem using the resonant-consistent method with He correlation energies, resonant-consistent method with higher ab-initio methods, and gradient descent optimization of basis and adaptive basis sets may be interesting.

Adaptive basis sets may be computed from these basis sets by tandem using the resonant-consistent method with higher ab-initio methods and gradient-descent optimization of basis for saving computational resources. For gradient-descent optimization is recommanded using a one-electron kinetic energies from equation fro expression a energy levels:

$$\hat{T} = \frac{h^2}{8\pi^2 m_e} * \psi_i \nabla^2 \psi_i. \qquad (11)$$

because in gradient-descent optimization are necessary energy members, that rise up energy levels with wavefunction exponents supralinearly to overcome too high exponents.

Description and Details of Implementation of the Algorithm in the Program for basis Set Optimization:

• First, a list of electrons, their positions, quantum numbers, spin-pairing, and bonding information, and the nucleuses of the source particle are generated. Next, grids with Slater-type orbitals (STOs) are generated. The effective nuclear charge $Z_{eff\ rel}$ for computation of its exponents is set according to relativistic corrections [3] to

$$Z_{effrel} = Z \cdot \sqrt{(1 - (Z\,(e^2/(2\epsilon_0 hc))/n)^2)} \qquad (12)$$

according to equation (9). In the case of polar compounds, the electron density of bonding electrons is moved to the bonding orbital of the electronegative second atom according to the Pauling formula [13]:

$$\delta = 1 - exp((\chi_A - \chi_B)^2/4), \qquad (13)$$

• where δ is the partial charge of the first atom, χA and χB are the electronegativities of the first and second atoms.
• Next, grids with spatial probability densities of electrons from these generated STOs are generated.
• Next, effective lengths of basis for computing integrals of nucleus attractions to centroid nuclei of electrons (firstly by numerical integration, in next iterations according to equation (9)) are generated. Integrals of nuclear attraction between nuclei and electrons are computed and summarized on the diagonal of the empty matrix of nuclear attraction integrals. The potential calculation uses the equation

$$\hat{V} = -\frac{e^2 Z}{4\pi\epsilon_0}\left\langle \psi_i \middle| \frac{1}{R} \middle| \psi_i \right\rangle, \qquad (14)$$

• where R is the electron – nucleus distance.
• The Coulomb repulsion integrals between individual electrons and the matrix of Coulomb integrals are integrated using the equation

$$V = \frac{e^2}{4\pi\epsilon_0}\left\langle \psi_i\psi_i \middle| \frac{1}{R} \middle| \psi_j\psi_j \right\rangle. \qquad (15)$$

• In the case of paired electrons on the same atom, the approximation of correlation energy from the Helium atom model is subtracted.
• Exchange integrals between individual electrons in systems with chemical bonds are integrated using a suitable approximation, and the matrix of exchange integrals is calculated next using the equation

$$V = \frac{e^2}{4\pi\epsilon_0}\left\langle \psi_i\psi_j \middle| \frac{1}{R} \middle| \psi_i\psi_j \right\rangle, \qquad (16)$$

• where ψ_i and ψ_j are wavefunctions of the i-th and j-th electrons.
• The kinetic energy integrals and the matrix of kinetic integrals are calculated according to the equations:

$$\hat{T} = \frac{h^2}{8\pi^2 m_e} * \psi_i \nabla^2 \psi_j \text{ and } \hat{T} = \frac{h^2}{8\pi^2 m_e} * \frac{Z \cdot Z_{eff}}{n^2} \qquad (17)$$

- from the virial theorem and Rydberg energy levels for one-electron energies, where h is the Planck constant, m_e is the electron mass, and ∇ is the nabla operator, a is the Bohr radius Z_{eff} is the effective nuclear charge and n is the main quantum number.
- The matrix of attraction integrals between nuclei and electrons, the matrix of coulombic integrals, the matrix of exchange integrals, the matrix of kinetic energy integrals, and the correlation matrix (which can be computed, for

example, from the PBE density functional are summed to calculate the matrix of energies of basis functions, and then its eigenvalues are calculated [12]. The lowest eigenvalue is added to its rows sums to express the energies of individual basis wave functions. Next, the overall non-orthonormalized Hamiltonian of the system is computed by summing the diagonal and upper diagonal parts of the basis set energies matrix.

- If the system Hamiltonian sufficiently matches the previous Hamiltonian, the computation is terminated. If not, new values of Z_{eff} are calculated using equation (10) as the energy of the basis, and the sums of the corresponding electron rows in the matrix of energies of basis functions and the lowest eigenvalue. The calculated value of Z_{eff} is used to calculate the new basis wave functions for the next iteration. The coefficients a (new/old ratios) in systems with maximal second quantum numbers 1, 2, 3, and 4 are 0.5, 0.25, 0.125, and 0.0625, respectively.
- In the developed program, a method for optimizing the PBE density functional parameters via a variational quantum eigensolver is implemented [14].

A variational quantum eigensolver algorithm (quantum simulator version):

- If the desired accuracy of wave functions is not achieved in the case of molecules, the previous procedure can be iteratively repeated for the variational quantum eigensolver (VQE) algorithm to optimizing parameters of PBE density functional. The procedure is as follows:
- The quantum circuit for the variational quantum eigensolver (VQE) is constructed for the desired depth of connectivity. The count of qubits in this circuit is equal to the count of electrons in the system, and quantum connections are set between the qubits representing electrons whose distance of the center of mass has not exceeded a specified limit.
- For the given molecular system, the first set of energy levels of the molecular system is calculated according to points 1-8 for the first set of pre-calculated Z_{eff}, including the influence of the PBE density functional with parameters for homogeneous electron gas.
- For the given molecular system, the second set of energy levels of the molecular system is calculated according to points 2-8 for the first set of pre-calculated Z_{eff}, including the PBE density functional with parameters for the Lieb-Oxford bond condition.
- The initial set of probability coefficients for the second set of wave function lengths has values 1 for electrons with lower energy levels for the Lieb-Oxford bond condition of the PBE density functional and 0 with more negative exchange-correlation energy for homogeneous electron gas conditions of the PBE density functional.
- Subsequently, operators of influence of PBE density functional parameters for individual electrons are calculated from the differences between the first and second sets of energy levels.
- These negatively taken probability coefficients are then transformed by the Jordan-Wigner transformation and scaled in the range of states 0 for lower energy with the first PBE density functional (for homogeneous electron gas) and 1 for lower energy with the second PBE density functional (with Lieb-Oxford bond conditions). From this energy to probability scale is taken too ansatz in next iterations. In subsequent iterations of calculations, calculated values of energy levels are converted to the specified scale from 0 to 1. Furthermore, these probabilities are embedded into Pauli matrices as an ansatz on the input qubits of the quantum computational circuit. The specificity of the Bravyi-Kitaev transformation is the subsequent suppression of long-range quantum entanglements, which can be advantageous compared to the Jordan-Wigner transformation.
- The prepared ansatz is applied to the qubits, and their state is measured.
- New probability coefficients influencing exchange-correlation energy are calculated from the ratios of the count of measured values of 1 and 0 on qubits to the total number of measurements, summing these ratios for atoms corresponding to qubits and by this way too new parameters of PBE density functionals as a linear combination of parameters for homogeneous electron gas and Lieb-Oxford bond condition in computed ratios.
- Steps 14-17 are iterated until convergence is achieved – appropriate stabilization of the system's Hamiltonian or until the maximum count of iterations is reached, and Z_{eff} are captured, and final PBE density functional parameters and system Hamiltonian are computed.

Practical Implementation in C++

For the implementation of this algorithm, a highly optimized C++ program "Basis set orbital 1.8" was created under the Apache license version 2.0 [15]. This program and its integral engine allow using 8 processor cores and vector instruction sets. For the quantum simulator, the MicroQiskit library is used. The program includes internal optimizations such as:

- Non-sign variable data types for using in cycles subscripts,
- Using analytical solutions of integrals,
- Using the same values of integrals for spin-paired orbitals in closed shell chemical systems and corresponding memory usage saving,
- Avoiding non-ordinary access to RAM,
- Using lower resolution of the basis 3D grids and detecting of a integration area for multiple integrals, than for simple integrals (function of square root of full resolution of 3D grid),
- using Gaussian elimination to triangle shape of matrix for diagonalization matrices and computing matrix eigenvalues.

Results and Discussion

Elements and Cations

The results for first 10 elements and its ionic species were computed with grid resolution 301 pixels per side in space of 10 atomic units of basis cube side. The results convergence criteria were 0.001 of absolute value of Hamiltonian

difference between iterations and 50 of max additional iterations.

The control sums of Hamiltonians for all first 10 elements, their cations, and first anions are given in Table 1 with comparison to experimental ionization energies sums and the shielding coefficients for these elements in the formof Z_{eff}/Z from electron oscillation energies are in Table 2 [16].

In these results, it is shown that the simple Slater-type orbitals are not suitable for the description of electron structure of anion species, which need diffuse functions. For closed-shell atoms and cations, the results are very precise, and the basis set well describes their electronic structure. For open-shell atoms and cations, the computed overestimated Hamiltonians may be greater due to non-involving the orthonormalization of basis sets and small integration errors.

	Ionization degree									
Element	-1	0	1	2	3	4	5	6	7	8
H	0.8095	1.0083								
He	0.8505	0.9972	1.0027							
Li	0.1970	1.0113	1.0138							
Be	0.3780	0.9604	1.0878	1.0132						
B	1.1467	0.9951	0.9539	1.0158	1.0077					
C	1.1608	1.0762	1.0210	0.9509	0.9904	0.9997				
N	1.1383	1.1053	1.0262	0.9735	0.9455	0.9808	0.9901			
O	1.1108	1.0761	1.0489	0.9874	0.9588	0.9403	0.9707	0.9791		
F	1.0220	1.0620	1.0320	1.0095	0.9556	0.9256	0.9340	0.9597	0.9671	
Ne	0.2690	0.9738	1.0215	0.9959	0.9768	0.9289	0.8587	0.9268	0.9481	0.9543

Table 1: The Ratios of Computed Hamiltonians and Experimental Sums of Ionization Energies for First 10 Elements and their Ionic Forms [16]

Excited States and Non-Polar Molecules

Results for basis sets of s to p excited states of Beryllium, Boron, and Carbon for the same parameters as base states were computed and compared with states energetic sums of Hamiltonians for base states of these elements. Computed excited energy levels were changed in comparison to base state: for Beryllium by -0.192 eV, for Boron by -28.672 eV, and for Carbon by 0.43 eV. The discrepancies may be caused by uncertainties in integrals.

	Electron number according to building rule									
Element	1	2	3	4	5	6	7	8	9	10
H	0.9973									
He	0.8938	0.8938								
Li	0.8178	0.8229	0.5589							
Be	0.8251	0.8251	0.8009	0.8009						
B	0.7774	0.7820	0.7446	0.7460	0.5680					
C	0.7498	0.7541	0.7280	0.730	0.5726	0.5725				
N	0.7204	0.7243	0.6844	0.6859	0.5487	0.5486	0.5486			
O	0.7318	0.7358	0.6375	0.6387	0.5236	0.5236	0.6564	0.6577		
F	0.7463	0.7503	0.6012	0.6022	0.5059	0.6171	0.6182	0.6171	0.6182	
Ne	0.7625	0.7625	0.5486	0.5486	0.5628	0.5628	0.5625	0.5625	0.5625	0.5625

Table 2: Shielding Coefficients (Z_{eff}/Z) for STO Atoms basis Sets

Next, the basis of the reaction coordinate of the H_2 molecule was computed with a resolution of 301 pixels per side and the same other parameters as atoms. In this result, the PBE density functional optimized for the Lieb-Oxford bond condition is involved [12].

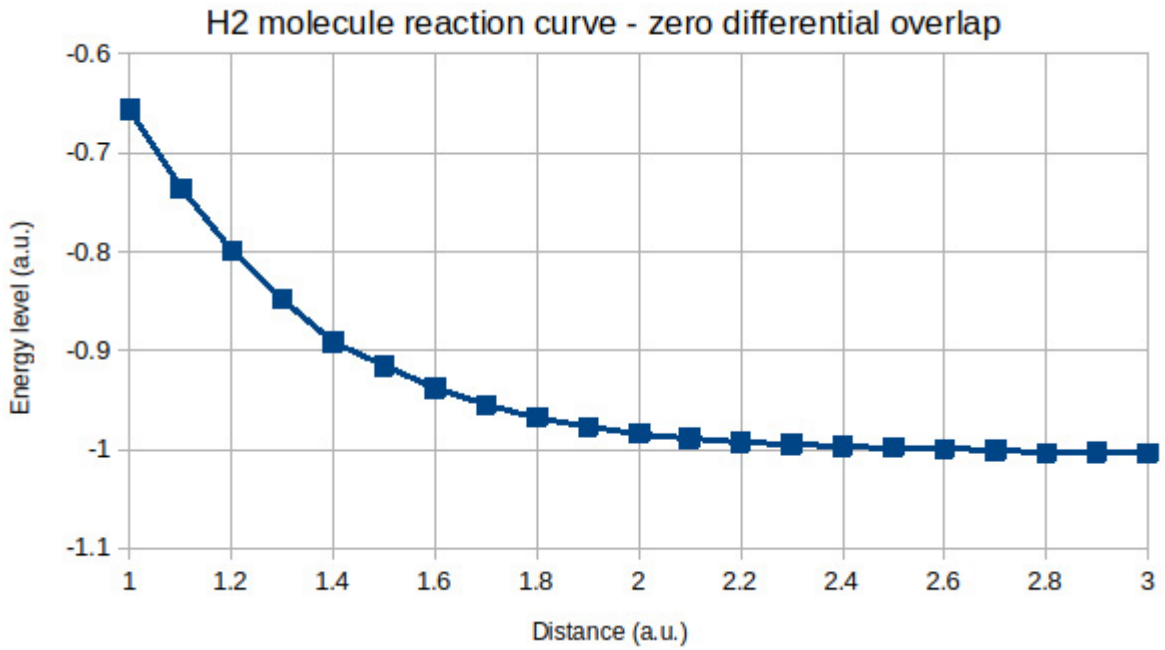

Figure 1: H_2 Molecule Control Sum of Hamiltonians Computed from Basis Functions (Atomic Orbitals) with Zero Differential Overlaps – ZDO Approximation.

The control Hamiltonian energy sums for H_2 are presented in Figure 1 for raw basis sets without any basis mixing (Hartree–Fock (HF) in a non–self-consistent form). The reaction energy from this sums is computed around 0.1 eV and the bond length around 2.8 Bohr radius.The experimental values are 4.5 eV and 1.35 a.u. [16]. The effective length of the H_2 basis is about 1.40-1.25 Bohr radius between 1.2-2.8 Bohr radius of bond length distance. The errors are caused by underestimating the bonding energy from Hartree–Fock (HF) in a non–self-consistent form. For a better description of the H_2 bonding curve, a combinations of atomic orbitals into molecular orbitals are necessary. The effective nuclear charge, or exponent, of the s1 Slater-type basis function was found to be 0.733 for a distance of 1.4 Bohr radii between the hydrogen atoms. In a study by Dunning et al. an exponent of 0.728 was proposed for the s1 Slater-type orbital, reinforced by a p-polarization function, for the H_2 molecule [6]. The effective nuclear charge is getting closer to 1 for higher inter-atom distances. A comparison of these values reveals that the proposed resonant-consistent algorithm is invariant for the H_2 molecule with respect to the localization of bonding electrons between bonded atoms, due to the cancellation of the influence of bonding and kinetic energies on the exponents in the energy minima.

Computations of he with PBE Correlation Energy

Next, computations of He were performed using a forked version of the basis set orbital, with exchange-correlation energies treated solely from the PBE density functional (not from empirical truncation of Coulombic integrals). The results were very similar to those obtained with the standard version of the program. After self-interaction error corrections, the Hamiltonian was 78.9561 eV, and the effective nuclear charge ($Z_{eff\ rel}$) relative to the real nuclear charge (Z) was 0.8912. The PBE functional, which was derived for homogeneous electron gas and two-electron ions was employed with parameters optimized for these systems [12]. The parameters of grid and simulation were the same, as for simulation of Helium with standard version of basis set orbital with generalized Helium correlation energy. The experimental value of Helium atom energy is 79.005 eV [16].

Computations of CH Radical and C_2H_2 Molecule

Next, computations of the CH radical and C_2H_2 molecule were performed in symmetry-broken spin states with parameters: 301 pixels per grid side, 10 Bohr radius of grid cube side and 100 of maximal additional iterations. For these computations, the PBE density functional optimized for parameters between homogeneous electron gas and Lieb-Oxford bond condition was used, employing a parametric expression of the Hamiltonian, finding connections between parameters, and solving by variational quantum eigensolver (VQE) [12,14].

This test was conducted using forked versions of the basis set orbital in three cases: a) without added PBE density functional, b) with added linearly optimized density functional, and c) with standard version of program with added VQE-optimized density functional only for molecules. The control sums of Hamiltonians were computed for the CH radical in cases radical in cases a) -1109.41 eV, b) 1111.93 eV, and c) -1129.98 eV, and for C_2H_2 in cases a) -786.521 eV, b) -792.665 eV, and c) 802.763 eV. For an accurate description of the electronic structure of these species, a basis set mixing algorithm like the Hartree-Fock method and eliminating the correlation energy is necessary. The results

show that the VQE algorithm successfully optimizes the PBE density functional, which describes the bonding correlation energy that influences the basis functions. The spin configurations of C_2H_2 molecule take not a ground state due to anti-phase configuration of px electrons.

Pi Electron Structure and Spectral Line

From the pi electron structure calculated by the Hückel method from pi electron exchange integrals for delocalized pi electrons of C_2H_2 with using the PBE exchange-correlation energies optimized by VQE, the spectral line with 165.7 nm (from sums of pi electron exchange integrals) was computed.

This spectral line for photolysis of ethyne with 171 nm was confirmed in a study, indicating good separation of processes of pi bonds transition to antibonding state and cancellation of other bonds [18]. For linearly optimized PBE and without PBE density functional, the energies of this spectral line were scattered. The symmetry theory may be used for symmetry-broken basis by combining it into symmetric basis, which are linear combinations of basis with different shielding coefficients and for various symmetry-broken states or determining averages of its Z_{eff}.

Discussion

The results for elements 11-118 were computed with a grid resolution of 301 pixels per cube side in space of 20 atomic units per cube side (elements 11-36) or 30 atomic units per cube side (elements 37-118). The convergence criterion was 0.0001 of relative value of Hamiltonian difference between iterations and 100 max iterations. Convergence was most commonly achieved for heavy species.

The described algorithms for optimizing basis sets depend on the right shape of atomic orbitals and evaluation of correlation energy, which must be sent back to computations. Ratios of computed non-orthonormalized and experimental Hamiltonians near 1 indicate good quality of the computed basis, and this was achieved with $Z < 29$ for majority of elements. The electronic structure of these species is expressible in terms of Slater-type orbitals or polarized Slater-type orbitals with generalized Helium atom correlation energy.

The order of effective average lengths of electron shells according to main quantum numbers was correct with minimal twisting of basis to other shells and minimal disrupting the order of sub-shells Z_{eff} rel according to the second quantum number (this is predictably altered due to differences in Coulombic integrals, spin-orbit coupling and grid integrating errors in kinetic integrals).

The s1 basis functions' effective lengths for elements with $Z > 92$ (U) is shorter, than the hyperfine structure constant (0.0072973525693 Bohr radius), which contributes to their nuclei instability due to electron-nucleus interactions from quantum chromodynamics.

The results of the semi-empirical level of the resonant-consistent algorithm harmonize with the proposed theory and are able to replace the Slater model of electron shielding. The resulting basis sets are portable to Gaussian basis sets derived from STO (sc-STO-xG), and for conversion, the ARO90 basis set can be used, for example. This process can be done by multiplying the exponents in TABLE III in the appendix of reference by $n/(Z_{eff\ rel})$, multiplying the contraction coefficients of seventh and higher odd n-1 Gaussian functions by -1, normalizing, orthonormalizing and saving the resulted basis [19,20].

Next, the basis sets optimization process can be completed via a higher level of resonant-consistent algorithm, applying the method of polarization function fitting (see Supporting information I) and gradient-descent method for Gaussian basis exponents and coefficients optimization according to system energy. Algorithms for this are currently being developed [6,7,21].

Additionally, a version of this optimization algorithm can be created for investigating high-temperature processes in atomic nuclei for nuclear physics.

A mathematical apparatus of the resonant-consistent algorithm can also be utilized to optimize multi-particle harmonic oscillators in string theory, leading to improved resolutions of condensed matter problems. These stringy oscillators are found in various phenomena, such as quantum Hall effects and bound/entangled states of fermions, including particles and quasi-particles with half-integer spin, like Majorana fermions, which facilitate electric current conduction in graphene. By combining both theories, researchers can investigate the Fermi surface of these oscillating systems through its dependence on magnetic fields. Furthermore, this approach enables the examination of the conformation of 2D strings that entangle particles through oscillating trajectory length corrections [22]. This principle bears a striking resemblance to the anti-de Sitter/conformal field theory (AdS/CFT) correspondence. In this framework, a quantum conformal field theory on one side corresponds to the arrangement of strings in anti-de Sitter space through a holographic principle, which highlights the similarity between the surface and interior of a black hole/brane.

Summary

In this paper, a new approach for optimizing STO basis sets is proposed and successfully verified. The results for all

elements, selected cationic species, excited states, and non-polar compounds are presented. This approach may be derived as a analytical and computationally efficient solution of minimizing system energy with remaining shape of basis functions for Slater type orbitals, polarized Slater type robitals and its combinations. The new basis sets are named resonant-consistent Slater-type orbitals (rc-STO).

Using the shielding-consistent procedure together with the polarization function fitting procedure is very interesting for creating adaptive basis sets for simulating conducting electric current via chemical species and their electrochemical properties due to good adapting to electric, magnetic, and other fields.

The resonant-consistent method may be used as initial step for creating adaptive basis sets. The full-optimized basis exponentst by gradient-descent method can be multiplied by ratios of exponents of adaptive resonant-consistent and atomic-centered resonant consistent basis. Today the author has a new versions of basis set orbitals with more saved computational resources and more options for a correlation energy expression for a production usage.

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