



Atomic Energy Calculations Using Gaussian Basis Functions



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Project Description

- Purpose is *very* accurate quantum calculations of atomic systems in ground and bound excited *s*-states using an improved basis function.
- An improved model can aid and verify very accurate experimental gas-phase electron spectra of these atomic systems.
- Calculated energy levels were previously accomplished by using exponentially correlated Gaussian basis functions, however, these functions have improper short-distance Kato cusps, too fast decaying long-range behavior of the wave function, and do not account for electrons occupying the same point space.
- The goal of this project is to correct the basis function to account for these phenomenon, obtain a more representative basis set, and obtain the lowest energy value with the least amount of functions necessary.

Potential Application

- Very accurate energy of atomic systems can aid experimentalists in experiment design and spectroscopists in spectra identification.

Methodology and Terminology

1. Description of Coordinate Systems

- Consider a *N*-particle atomic system, i.e. *N* - 1 = *n* electrons and a nucleus.
- The position vector, \mathbf{R}_i , of the *i*th particle is in Cartesian coordinates.
- The nucleus of the atom has mass, M_1 , charge, Q_1 .
- The electrons of the atom have mass M_2, \dots, M_N , and charge, Q_2, \dots, Q_N .
- The total mass of the system is $M_{\text{tot}} = M_1 + \dots + M_N$.

2. Non Born-Oppenheimer Approximation

- The center of mass motion of the atom can be separated out of the non-relativistic Hamiltonian.
- This separation results in two Hamiltonians: one for the **center of mass motion** and the other for the **internal motion of the electrons**.
- The center of mass motion is described by $\mathbf{r}_0 = \frac{M_1}{M_{\text{tot}}}\mathbf{R}_1 + \frac{M_2}{M_{\text{tot}}}\mathbf{R}_2 + \dots + \frac{M_N}{M_{\text{tot}}}\mathbf{R}_N$
- With this the index on particles is shifted.
- The distance between the nucleus and an electron is $\mathbf{r}_{i-1} = -\mathbf{R}_1 + \mathbf{R}_i$.
- The distance between any two electrons is $\mathbf{r}_{ij} = |\mathbf{r}_j - \mathbf{r}_i|$.

3. Internal Hamiltonian

$$\hat{H} = -\frac{1}{2} \left(\sum_{i=1}^n \frac{1}{\mu_i} \nabla_{\mathbf{r}_i}^2 + \sum_{\substack{i,j=1 \\ i \neq j}}^n \frac{1}{m_0} \nabla_{\mathbf{r}_i} \cdot \nabla_{\mathbf{r}_j} \right) + \sum_{i=1}^n \frac{q_0 q_i}{r_i} + \sum_{i>j=1}^n \frac{q_i q_j}{r_{ij}}$$

- The mass of the nucleus for the internal system is m_0 .
- The reduced mass of the electron is $\mu_i = m_0 m_i / (m_0 + m_i)$ and is now called the **pseudoelectron**.
- The charge on the nucleus is q_0 and the charge on the **pseudoelectron** is q_i .
- The first term in Hamiltonian is the Kinetic energy of the **pseudoelectron**.
- $\nabla_{\mathbf{r}_i}$ is the gradient operator in a vector form. **Note: prime indicates vector transpose**
- The second term is the mass polarization term.
- The third term is the Coulombic interaction between the nucleus and the **pseudoelectron**.
- The fourth term is the Coulombic interaction between two electrons.

Methodology Continued

4. Variational Principle, Total Atomic Wave Function, and Total Energy

- The variational principle states that the expectation value of the Hamiltonian operator over all space, $d\tau$, including spin, divided by the average value of the total atomic wave function, Ψ , will always be greater than the lowest energy, E_0 , of the system.

$$\frac{\int \Psi^* \hat{H} \Psi d\tau}{\int \Psi^* \Psi d\tau} > E_0$$

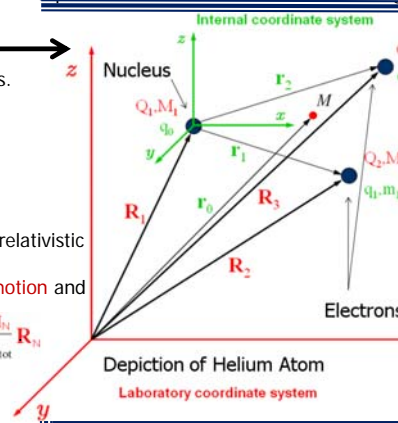
Note: asterisk stands for complex conjugate

- Since the Hamiltonian is independent of the spin of the particle, spin of the system can be eliminated from the wave function, Ψ , through spin integration, and that results in a spin free spatial wave function, $\psi(\mathbf{r})$, and is approximated by using the superposition principle.

$$\psi(\mathbf{r}) = \sum_{k=1}^K c_k \hat{Y} \phi_k(\mathbf{r})$$

$$\mathbf{r} = \begin{pmatrix} r_1 \\ r_2 \\ \vdots \\ r_n \end{pmatrix}$$

- \mathbf{r} is a vector of **pseudoelectron** coordinates.
- c_k is the linear coefficient of the wave function expansion.
- \hat{Y} is a permutational symmetry projector which effectively accounts for the phenomenon that electrons are indistinguishable and is specific for a particular system.



- $\phi_k(\mathbf{r})$ is the basis function.
- K is an index of basis Functions.
- The Variation Principle leads to the Secular equation. $(H - \epsilon S)c = 0$
- H and S are $K \times K$ hermitian matrices.
- c is a vector of linear coefficients, c_k , in the wave function expansion with matrix elements $H_{kl} = \langle \phi_k | \hat{H} Y | \phi_l \rangle$ and $S_{kl} = \langle \phi_k | \hat{Y} | \phi_l \rangle$ in bracket notation.
- Note: dagger indicates transpose follow by complex conjugation.
- ϵ is the energy eigenvalue of the problem and is minimized by using simultaneous diagonalization of the Hamiltonian and overlap matrices.
- Analytic energy gradient is also utilized to optimized the basis functions.

5. Basis Functions and Matrix Elements

$$\phi_k = \exp[-\mathbf{r}^T \mathbf{A}_k \mathbf{r}] \quad \psi_k = \mathbf{r}^T \mathbf{W}_k \mathbf{r} \exp[-\mathbf{r}^T \mathbf{A}_k \mathbf{r}]$$

- Previously [1], explicitly correlated Gaussian (ECG) basis functions, ϕ_k , were utilized.
- \mathbf{A}_k is a $3n \times 3n$ symmetric positive definite matrix of α -Gaussian parameters and is ensured positive definite by using a Cholesky factorization.
- Explicitly correlated Gaussian functions are adequate for describing *s*-states of atoms because Gaussians are spherically symmetric, however, these functions have improper short-distance Kato cusps, too fast decaying long-range behavior of the wave function, and do not account for electrons not occupying the same point space.
- Proposed is to pre-exponentially correlate the ECS basis with a factor of $r_{ij}^2 = |\mathbf{r}_j - \mathbf{r}_i|^2$ which will allow the basis function to go to zero when the electron occupy the same point same and, therefore, the new basis function is ψ_k .
- The r_{ij}^2 factor of new basis function, ψ_k , is written in the quadratic form.
- \mathbf{W}_k is a symmetric $3n \times 3n$ matrix consisting of 1 and -1 in appropriate places to yield the correct r_{ij}^2 factors.
- There are four integral types required: $\langle \phi_k | \phi_l \rangle$, $\langle \phi_k | \hat{H} | \phi_l \rangle$, $\langle \psi_k | \psi_l \rangle$, $\langle \psi_k | \hat{H} | \psi_l \rangle$
- Note: tilde indicates permutation

Results

- The convergence of the total variational energy of the ground state of the helium atom (with an infinite mass of nucleus), lithium atom (isotope 7), and beryllium atom (isotope 9), with the number of functions in the basis set and a comparison with the best literature values to date. The number of the functions with and without the r_{ij}^2 factor are shown. The energy values are in Hartrees. Significant result is outlined.

Note: 1 Hartree = 27.2107 eV (electron Volts) = 219474.63 cm⁻¹ (wavenumbers).

Atom	No. of functions	No. of functions without r_{ij}^2	No. of functions with r_{ij}^2	Energy
He	40	35	5	-2.9037078029
	80	68	12	-2.9037231974
	120	94	26	-2.9037242693
	160	122	38	-2.9037243533
	200	148	52	-2.9037243689
	240	174	66	-2.9037243735
	280	195	85	-2.9037243765
	300	210	90	-2.903724376612
	320	220	100	-2.903724376905
	340	232	108	-2.903724376936
1500 [1]	1500	0	-2.903724377034	
Li	300	145	155	-7.477447159115
	500	223	277	-7.477450867519
	700	304	396	-7.477451612675
	10000 [2]	10000	0	-7.4774519307
Be	200	59	141	-14.666042640791
	400	105	295	-14.666412550203
	500	120	380	-14.666422681409
	10000 [3]	10000	0	-14.666435504

Conclusion and Further Directions

A mixture of ECGs and pre-exponentially correlated ECGs are used in calculated the ground state energy to account for the fact the electrons do not occupy the same point space. There are two important results. The first, for helium, the combined basis set size of 280 functions reproduces the energy obtained with 1500 basis functions to 9 significant digits. The second is that as the number of basis functions is increased so is the percentage of the usage of functions with the r_{ij}^2 factor. This indicates that this function is important in describing the total energy of the system. The test clearly shows that the basis set that combines the ECGs with the r_{ij}^2 factor performs even better than ECGs without the factor. Calculations are currently on going for lithium atom and beryllium atom. This method can be applied to calculate excited state of these systems as well as ground and excited states for other atoms in *s*-states.

References

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