

Computational Investigation of e^+ BeO system: Atom-centered Gaussian type positronic basis set development for low-cost calculations

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1. ABSTRACT

The positron binding to the BeO molecule was computationally investigated using *ab initio* quantum chemistry methods. In order to calculate the positron density distribution of the e^+ BeO system, 6s6p Gaussian-type atom-centred positron basis sets were optimized for oxygen and beryllium at the Hartree-Fock (HF) level of theory. The calculated total energy of the e^+ BeO system is in agreement with the calculations done in literature at higher levels of theory. Further, we computationally investigated the positron density distribution of the e^+ BeO system by reducing the size of the positron basis sets. Accordingly, we found that qualitatively reliable calculation can be done by keeping the 6s6p optimized positron basis set at the most electronegative site: in our case oxygen site without the positron basis set at the beryllium site. This work suggests a qualitatively reliable low-cost computational method which can be applied for e^+ bound to large molecule systems of ionization energy (IE) > 6.8 eV.

Keywords: positron, annihilation, basis set, GAMESS-NEO.

1. INTRODUCTION

The existence of the anti-particle of the electron; the positron was experimentally discovered by C. D. Anderson in 1933 [1]. When a positron interacts with an electron it annihilates by emitting two gamma rays where each gamma ray carries the energy of 511 keV [2]. Further to the direct annihilation process, a bound state of electron-positron called positronium (Ps) was discovered experimentally in 1945 [2,3]. The bound state binding energy of the Ps is 6.8 eV and Ps undergoes annihilation by emitting gamma rays in less than 100 ns of lifetime [3]. After the 1940s, positron-electron annihilation studies led to the understanding of the properties of solids [3]. Today, positron-electron annihilation is used for Positron Emission Tomography (PET) in medical imaging to investigate the metabolic activity of the human. In the material science field, positron annihilation spectroscopy is mostly used for semiconductor defect identification [4,5]. Though there are many experimental studies on low energy positrons interaction with atoms and molecules in the gas phase [6-15], few theoretical investigations of positron binding to monoatomic, di atomic and small molecules are found in literature [16-23]. Positron binding energy and annihilation properties were investigated of PsH, PsLi⁺, and

e^+ LiH systems using Explicitly Correlated Gaussian (ECG) functions [16-18]. Quantum Monte Carlo (QMC) methods are used to calculate the positron affinity of e^+ LiH, e^+ BeO, OHPs., CHPs., and NH_2 Ps systems [19-20]. In 2012, C. Swalina *et. al.* implemented the Nuclear Electronic Orbital (NEO) method to obtain the positron binding energy of the e^+ LiH system [21]. Positron interaction with moderate-size molecules such as Formaldehyde, Urea and Acetone at the Configuration Interaction (CI) level of theory was investigated [22,23]. In these cases, only one large size of positron basis set including diffuse functions was used at the center of mass of each molecule. Due to the higher computational demand, the above methods cannot be expanded to the bigger e^+ -molecule systems [22]. Further, optimizable positron basis centers are not feasible for investigating the interactions of positrons with large molecules, particularly those with no obvious axis of symmetry.

According to past studies, positron-electron correlation effects need to be considered when modelling proper positron-molecule interactions [16-23]. In e^+ Li system, Li has an ionization energy of about 5.4 eV [16]. Hence, when the positron interacts with the Li atom, the loosely bound electron and the positron are more likely to bind and make Ps cluster. It is essential to consider positron-electron correlation when calculating the ground state energy of e^+ Li system in order to obtain accurate results [16-18]. Similarly, atoms and molecules which have the first ionization energy (IE) less than the positronium formation energy; 6.8 eV, the higher correlation effect of positron-electron is needed to cooperate [24]. When the $\text{IE} > 6.8$ eV, the electron and positron correlation is weaker. Hence, the formation of Ps is less probable [25]. Such e^+ -molecule system is more likely to behave as a weakly bound positron orbiting at some distance from the remainder of the system. In order to model such a system qualitatively, a low-cost computational method such as HF level of theory is suggested in this work. However, proper inclusion of positron wavefunction is required in order to obtain the e^+ -molecule ground state energy, positron density distribution and positron-electron density (contact density) distribution. In this work, we investigated positron binding energy, positron density distribution and contact density distribution of the e^+ BeO system at the NEO-HF level of theory. In order to obtain the qualitatively acceptable positron-molecule interaction at a low level of theory, more positron basis centers are needed. Therefore, we optimized 6s6p atom-centered Gaussian-type positron basis sets for Be and O atom centers. Having moderate-size positron basis sets on both atom centers were sufficient and flexible enough to give qualitatively correct positron density and positron-electron density distributions. In this study, we show that computationally low-cost calculation can be done using a single positron basis center at the most electro-negative atom site. Accordingly, we propose a qualitatively acceptable low computational demand calculation method for larger positron-molecule systems which have $\text{IE} > 6.8$ eV.

2. METHODS

The e^+BeO system consists of one positron, twelve electrons ($N_e=12$) which are treated as quantum particles and two classical nuclei; Be and O. The Born-Oppenheimer Hamiltonian of such a particle system (in atomic units) can be written as follows:

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_i^{N_e} \nabla_i^2 - \frac{1}{2} \nabla_p^2 - \sum_i^{N_e} \frac{Z_{Be}}{|r_i^e - r_{Be}^c|} - \sum_i^{N_e} \frac{Z_O}{|r_i^e - r_O^c|} + \frac{1}{2} \sum_{i \neq j}^{N_e} \frac{1}{|r_i^e - r_j^e|} \\ & + \frac{Z_{Be}}{|r^p - r_{Be}^c|} + \frac{Z_O}{|r^p - r_O^c|} - \sum_i^{N_e} \frac{1}{|r_i^e - r^p|} \end{aligned} \quad (2.1)$$

Here, indices i , and j refer to electrons and r_i^e - i^{th} electron coordinate
 r^p – positron coordinate
 r_{Be}^c – coordinate of the classical nucleus Be
 r_O^c - coordinate of the classical nucleus O
 Z_{Be} and Z_O – charge of the Be and O respectively.

The many particles of HF wavefunction of the positron-molecule system (Ψ_{tot}) can be written as

$$\Psi_{tot} = \Psi^e(r^e) \Psi^p(r^p) \quad (2.2)$$

where $\Psi^e(r^e)$ and $\Psi^p(r^p)$ are anti-symmetrized electronic and positronic wavefunctions and r^e and r^p represent the spatial coordinates of the electrons and the positron, respectively [26,27]. The atom-centered positron single-particle wavefunction is expressed in terms of a linear combination of Gaussian-type orbitals, centered at the Be and O nuclei. For a positron at (r^p, θ, φ) :

$$\Psi^p(r^p, \theta, \varphi) = A \sum_{\mu=Be,O} \sum_{l,m} Y_l^m(\theta_{\mu p}, \varphi_{\mu p}) \sum_i^N C_{\mu l m i} r_{\mu p}^l e^{-\alpha_{\mu l i} r_{\mu p}^2} \quad (2.3)$$

where $r_{\mu p}$ is the distance between the atomic nucleus and the positron and A is the normalized constant. $Y_l^m(\theta_{\mu p}, \varphi_{\mu p})$ is the spherical harmonic function which depends on angular quantum numbers l and m . N is the number of Gaussian primitives for a single spin-orbit [28]. Here, $\{C_{\mu l m i}, \alpha_{\mu l i}\}$ is called the Gaussian Basis set which is not implemented for positrons in quantum computational packages yet. However, the General Atomic and Molecular Electronic Structure Systems – Nuclear Electronic Orbital (GAMESS – NEO) framework [26-27], can be used to study the positron-molecule interaction.

As there was no atom-centered positron basis sets developed previously, in this work we have optimized the atom-centered Gaussian type positron basis sets for Be and O atoms centers in the e^+BeO system. Here, we optimized even tempered positronic basis sets one

at a time for both atom centers. Initially, we arbitrarily selected the same Gaussian basis set $\{C_{\mu l m_i}, \alpha_{\mu l i}\}$ for both atom centers. Then calculated the energy of the e^+BeO system for different even-tempered basis set for one atom center while freezing the other basis set at the other atom center. When we reached to minimum energy of the system, then we optimized the other basis set while freezing the optimized basis set obtained from the previous step. The flowchart of the optimization of the positron basis set of a one-atom center is shown in the following Figure 1.

Here, all the positronic calculations were carried out at the NEO-HF level of theory for e^+BeO while 6-31+G(d,p) basis sets were used for electrons. The geometry optimization and the first ionization energy for the BeO system were carried out at the DFT-B3YLP level of theory with 6-31+G(d,p) electron basis sets. Finally, we obtained two different 6s6p type positron basis sets for each atom center which gives minimum energy for the e^+BeO system at the NEO-HF level of theory.

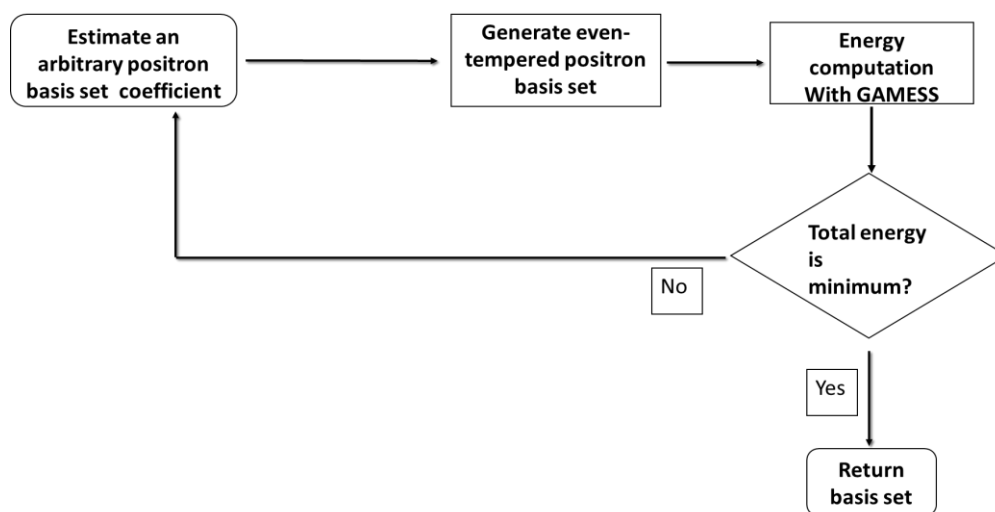


Figure 1:- Flow chart of finding of the best atom centered gaussian positron basis set

3. RESULTS AND DISCUSSION

The calculated IE of the BeO in this study (DFT-B3YLP/631+G(d,p)) was 10.1 eV which is in agreement with the experimental data [29,30]. As the IE_{BeO} is greater than the positronium binding energy (6.8 eV), the correlation between positron and electrons is not much prominent. Hence, the optimization of the positron basis sets was carried out at low computational demand NEO-HF level of theory for a qualitative study of the positron-molecule interaction of the e^+BeO system.

The minimum energy for the e^+BeO system was computed with various types of even-tempered positron basis sets for Oxygen and Beryllium with NEO-HF-level. Among them, the 6s6p positron basis sets were able to give the minimum total energy for the system. The obtained minimum energy was compared with the high computational

demand methods such as Variational Monte Carlo (VMC) method and Diffuse Monte Carlo (DMC) method in the literature [19]. Table 3-1 shows the energy values of the computational methods in different levels. All the energy is calculated in Hartree.

Table 3-1:- Ground state VMC, DMC and NEO-HF energies for e^+BeO system.

Level of theory	Total Energy (Hartree)
E_{VMC}	-89.3365 [19]
E_{DMC}	-89.8134 [19]
E_{NEO-HF}	-89.4263 [this work]

The proposed method in reference [19], used electron-electron and electron-positron correlations explicitly. However, the developed atom centered positron basis sets in this study well explained the positron wavefunction of the e^+BeO system with respect to the VMC method reported in [19] as lower total energy was obtained in this work.

In order to study the positron-molecule interaction, we developed necessary visualization tools for electron, positron and electroan-positron density distribution in 1D, 2D and 3D.

Figure 3-1 shows the normalized electron density distribution of the e^+BeO system which was obtained at the NEO-HF level with 631+G(d,p) electron basis sets. The higher electron density can be seen at the two nuclei of the system due to attractive forces between the electrons and the positive charge nuclei. The lower positron density distribution can be seen at the positively charged nuclei of the system due to the Coulomb repulsion between the positron and positively charged nuclei. But the higher positron density was obtained near the O site opposite to the Be atom center. Here, we used the developed 6s6p positron basis sets for both atom centers and the positron density was calculated at the NEO-HF level of theory. In the graph, the x-axis is shown in grid points where 10 grid points are equal to 1 A.U.

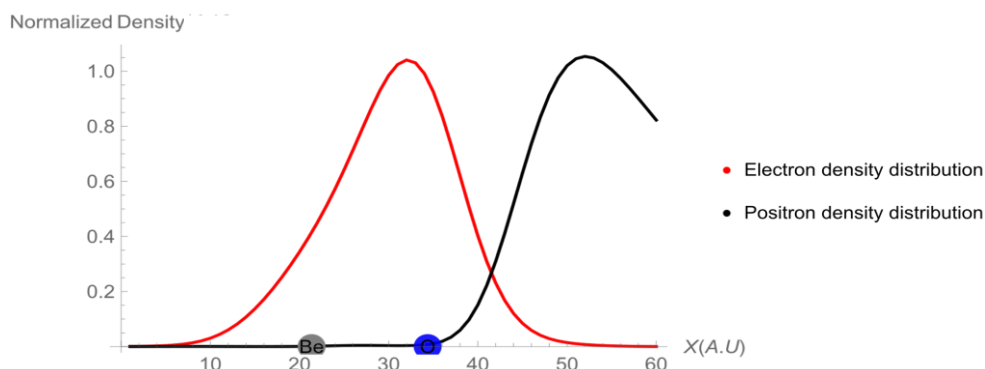


Figure 2:-1D electron and positron density distribution of the e^+BeO system

In order to understand the reason for getting higher positron density near the Oxygen site, we calculated the electrostatic potential of the BeO system at the DFT-B3YLP level with 631+G(d,p) electron basis sets. The electrostatic potential and the positron density distribution are shown in the Figure 3. Here, negative electrostatic potential is observed near the Oxygen, opposite to the Be atom center. The higher positron density is also

observed on the same side where the negative electrostatic potential is detected. Accordingly, the positive charge positron is more likely to be stuck in the negative potential well is the reason for getting higher positron density at the negative potential site of the e^+BeO system.

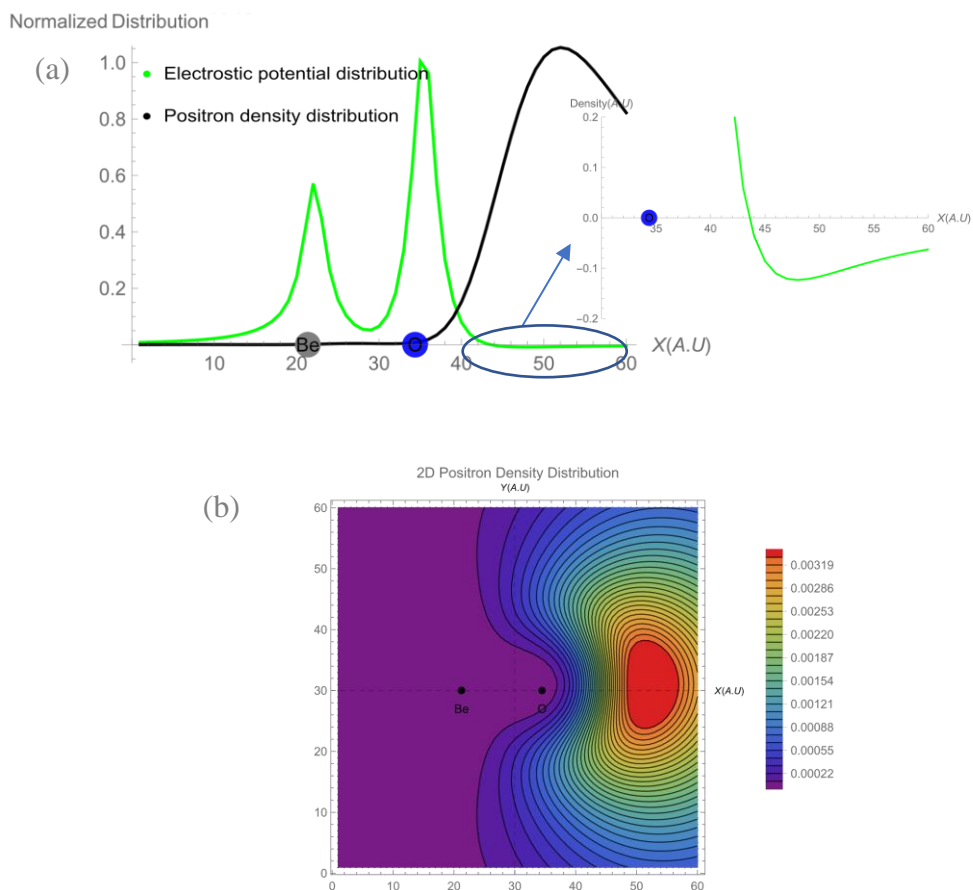


Figure 3:- (a) 1D electrostatic potential distribution and Positron density distribution, (b) 2D positron density distribution grid points 60x60 (3 x 3 a.u).

The calculated electron and positron wavefunctions were used to find the possible electron-positron annihilation site of the e^+BeO system. Here, we calculated the contact density; $|\Psi^e(r^e)|^2|\Psi^p(r^p)|^2$ in order to find the highest overlap between the electron and positron wave functions. The visualization of the contact density distribution is shown in Figure 4.

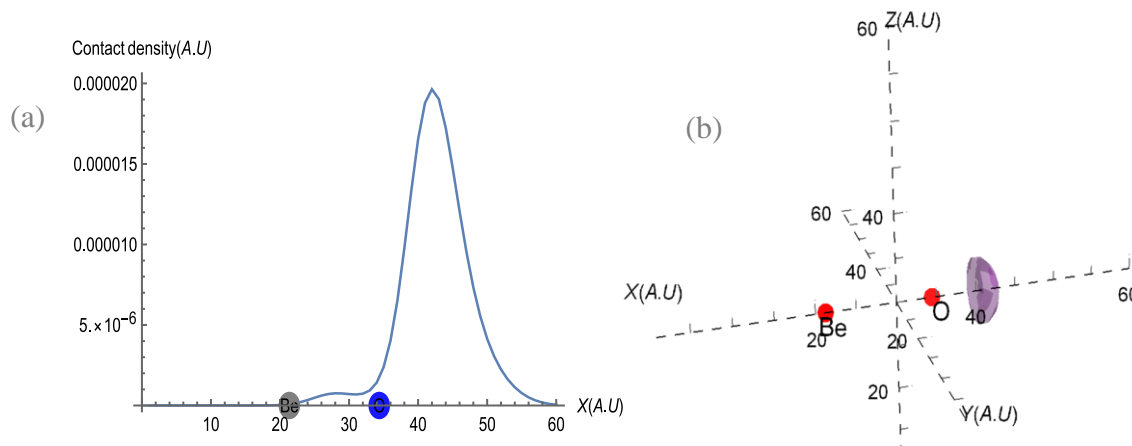


Figure 4:- (a) 1D contact density (b) 3D contact density of e^+BeO (contour:- 0.000018 a.u method: NEO-HF, Basis set: 6s6p on both atom centers, grid points 60x60x60 (3x3x3 a.u).

The highest contact density can be seen at the same site where the negative potential is obtained. Due to the highest overlap of the electron and positron wavefunctions at this site, there is a higher probability to positron annihilates with one of the electrons in this site.

According to the above results, the positron basis set (6s6p) at the Oxygen atom center must contribute to the positron density distribution significantly. Hence, we calculated the ground state energy, positron density distribution, and contact density distribution of the e^+BeO system with single positronic basis set (6s6p) at the O atom center. The total ground state energy of -89.4256 Hartree was obtained. The comparison of the contact densities obtained using 6s6p positron basis sets on both atom centers and only at the O atom center is visualized in Figure 5. The ground state energy is higher by 0.0007 Hartree in this case with respect to the ground state energy obtained with both positron basis sets Table 1.1.

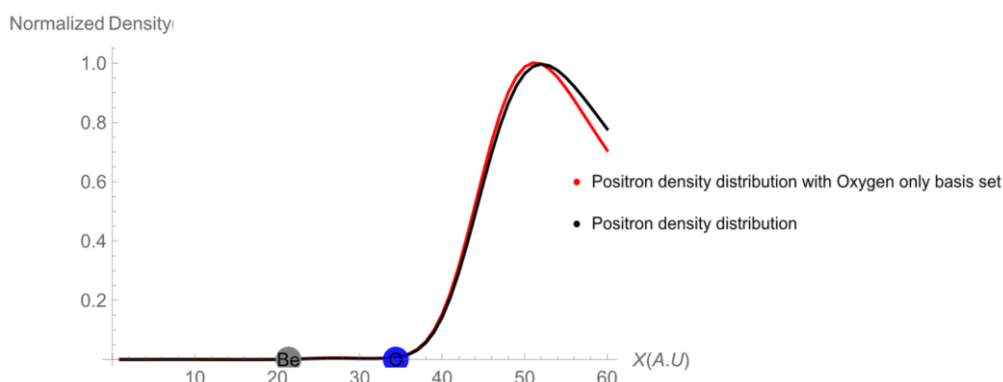


Figure 5:- 1D contact density of e^+BeO method:NEO-HF red- 6s6p positron basis set only at O, black- 6s6p positron basis sets on both atoms

The positron density distribution in both cases does not show significant differences. Hence, there are no significant changes in the contact density distribution as well. This suggests that qualitatively correct low-cost computational calculations can be done with positron basis sets at more electro-negative atom sites in e^+ -molecule systems.

4. CONCLUSION

We have developed 6s6p type atom centered positron basis sets for $e^+(\text{Be})$ and $e^+(\text{O})$. The ground state energy of the $e^+\text{BeO}$ system agrees with the most accurate calculation done with high computational cost in literature. The higher positron density and higher contact density were found near the Oxygen site opposite to the Be atom where at the same site we observed the negative electrostatic potential of the BeO system. Hence, the developed atom centered positron basis sets are well enough to explain the positron density and contact density distribution qualitatively at the NEO-HF level of theory. Accordingly, we have found that there is a higher probability of positron annihilating with one of the electrons near the O atom site. Further, we could do computationally lower demanding calculations having a properly optimized positron basis set (6s6p) only at the most electronegative atom site. This suggests one can study qualitatively correct calculations for larger positron-molecule systems of IE > 6.8 eV at the NEO-HF level with properly optimized atom centered positron basis sets.

5. ACKNOWLEDGEMENTS

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