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• Monte-Carlo configuration interaction applied to various positronic molecules.
• Compact correlated electronic-positronic wavefunctions obtained.
• Able to predict accurate positron affinities using off-the-self quantum chemistry basis sets.
• Multi-reference character of positronic wavefunctions evaluated and discussed.
*Graphical Abstract (pictogram) (for review)*
Positronic molecule calculations using Monte Carlo Configuration Interaction

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Abstract

We modify the Monte Carlo configuration interaction procedure to model atoms and molecules combined with a positron. We test this method with standard quantum chemistry basis sets on a number of positronic systems and compare results with the literature and full configuration interaction when appropriate. We consider positronium hydride, positronium hydroxide, lithium positride and a positron interacting with lithium, magnesium or lithium hydride. We demonstrate that we can capture much of the full configuration interaction results, but often require less than 10% of the configurations of these multireference wavefunctions. The effect of the number of frozen orbitals is also discussed.

Keywords: Positrons. Quantum Chemistry. Monte Carlo Configuration Interaction.

1. Introduction

Relativistic quantum mechanics predicted the possibility of a particle with the mass of the electron but opposite charge [1]. This positron was experimentally discovered by Anderson in 1932 [2] and can form short-lived complexes with matter: experimental evidence for a bound state of an electron and positron (positronium) was found in 1951 [3] and orthopositronium has a mean lifetime of the order of $10^{-7}$ seconds [4]. Gamma emission from the annihilation of positrons can be exploited for spectroscopy, for example to investigate the pore entrance size in silica films [5]. While positron emission tomography has important medical applications where gamma radiation is detected from the decay of positronium formed by positron emission from an injected radioactive tracer [6]. It is therefore of great interest to theoretically investigate whether a positron can form a stable complex with molecules to aid the understanding of positron behavior in matter.

The first theoretical demonstration that a positron could stably bind to an atom was due to Ore in 1951 for positronium hydride [7]. Later work often used the stochastic variational method (SVM) [8] to optimize correlated functions for the successful description of small positronic systems with the fixed-core approximation. For example, in Ref. [9] it was used to show that positronium hydride, $e^+\text{Li}$ and $e^+\text{Mg}$ are stable. Diffusion quantum Monte Carlo is another powerful approach that offers the prospect of modelling larger positronic systems, but with the requirement of the fixed-node approximation. This has been used, e.g., for accurate calculations of the positron affinity of lithium hydride and the weakly bound system of hydrogen cyanide with a positron [10].

Research has also turned towards configuration interaction methods: Ref. [11], for example, investigated this approach with the long-term goal of modelling heavier systems considered difficult with the SVM. There it was found that results were slowly convergent with respect to the angular momentum number of the Laguerre basis functions. Positron binding with group-II atoms was also found to be stable using configuration interaction [12]. Configuration interaction has also been used to show that positronic hydrogen cyanide is weakly stable [13]. While multireference configuration interaction using single and double substitutions for positronium halides has been implemented [14] and this has also been applied to atoms interacting with two positrons [15].

The approach of Monte Carlo configuration interaction (MCCI) [16, 17] iteratively constructs a configuration interaction wavefunction using a stochastic procedure that can, in principle, capture much of the full configuration interaction (FCI) wavefunction, but using only a very small fraction of the configurations. This approach has been applied to construct compact wavefunctions for a range of problems in quantum chemistry encompassing dissociation energies [18, 19], potential curves [20, 21], electronic excitations [22, 21], multipole moments [23] and hyperpolarizabilities [24]. The method has also been used with complex wavefunctions to study tunnel junctions [25]. An investigation of whether this technique can be adapted to efficiently model positronic systems is therefore timely. Computational quantum chemistry, as a well-established field, has many commonly available basis sets for atoms that are considered reliable. Investigations of positronic systems with configuration interaction often use semi-empirical terms in the Hamiltonian and specially constructed basis sets as it is found that functions with high angular momentum are needed and it is difficult to describe the system.
with atom-centred single-particle functions [26]. This can be attributed to problems describing cusps [27] due to the electron-positron interaction and the diffuse nature of positron orbitals [10] adds another challenge. Very large standard basis sets of quantum chemistry would therefore need to be used and would preclude the use of full configuration interaction or even large truncated configuration interaction calculations. We therefore investigate if, by adapting MCCI, we can stochastically construct an ab initio wavefunction that can describe a positronic system sufficiently well but uses a small fraction of the configurations necessary for FCI when using standard quantum chemistry basis sets. The majority of quantum-chemistry basis sets used in this work are available at the Basis Set Exchange [28].

In this letter we first describe the positronic MCCI approach then use positronium hydride as an initial test case where we compare the MCCI results with the literature and FCI. We next look at positron binding in the lithium atom and anion, then consider magnesium with a positron. The positron affinity of the lithium hydride molecule is then investigated and finally we calculate binding energies of positronium hydroxide.

2. Method

MCCI [16, 17] approximates the solution of the time-independent electronic Schrödinger in a given basis by usually beginning with a configuration formed from the occupied Hartree-Fock molecular orbitals. The configuration space is then increased by randomly implementing symmetry-preserving single and double substitutions. The Hamiltonian matrix is constructed, diagonalized and those new configurations with absolute coefficient $|c_i|$ less than $c_{\text{min}}$ in the resulting wavefunction are deleted. This can be run in parallel where retained configurations are shared between processors. The method is iterated until convergence in the energy is found to some tolerance and every ten iterations all configurations become candidates for removal.

For a molecule with one positron the Hamiltonian becomes

$$\hat{H} = \hat{T} + \sum_a \sum_{i<j} \frac{Z_a}{r_{ij}} + \sum_a \sum_i \frac{1}{r_{ai}} - \sum_i \frac{1}{r_{ip}}$$ (1)

where $\hat{T}$ is the kinetic energy operator, $a$ labels the atomic nuclei, $p$ the positron and $i$ and $j$ the electrons. $Z_a$ is the charge of nucleus $a$ and $r_{ij}$ is the distance between particles $i$ and $j$.

We modify the MCCI procedure to use this Hamiltonian and consider configurations comprised of a Slater determinant (SD) and a positronic orbital $\langle \phi(r_p) \rangle$. As part of this modification we therefore adapt the Slater-Condon rules for the construction of the non-zero Hamiltonian matrix elements

$$\langle SD_{k_1}\phi_m(r_p)|\hat{H}|SD_{k_2}\phi_n(r_p) \rangle$$

using the kinetic, potential and Coulomb integrals of the electronic Hartree-Fock molecular orbitals calculated with the COLUMBUS program [29]. When considering the constituent parts of the Hamiltonian the following modifications to the Slater-Condon rules of electronic structure calculations are required:

- One-electron terms

The SDs may have 0 or 1 difference while $m_1 = m_2$;

- One-positron terms

The SDs must be the same and there is a sign change for the potential integrals;

- Two-electron terms

The SDs may have 0, 1 or 2 differences while $m_1 = m_2$;

- Electron-positron terms

There is no restriction on the positronic orbitals and this becomes a one-electron integral for the SDs with operator

$$\sum_i \frac{\phi_m(r_p)\phi_n(r_p)}{r_{ip}}$$

which is calculated from the Coulomb integrals with a change of sign. Hence the SDs may have 0 or 1 difference.

3. Results

3.1. Positronium Hydride

We first test the MCCI procedure on a system comprising two electrons, a positron and a hydrogen nucleus: positronium hydride. The non-relativistic ground-state energy of the hydrogen atom is $-0.5$ Hartree and, by substituting the mass of the electron for the mass of the proton, that of positronium is $-0.25$ Hartree. Hence positronium hydride will be predicted to be stable if its energy is less than approximately $-0.75$ Hartree.

The first result to show that this system was stable found a binding energy of 0.07 eV [7]. The binding energy has been experimentally deduced [30] as $1.1 \pm 0.2$ eV. Perhaps the most accurate theoretical result [31] of $-0.789196740$ Hartree is in agreement with experiment and used the SVM with correlated functions to give rise to a binding energy of 1.07 eV.

We briefly mention some of the other theoretical work undertaken on this system. Explicitly correlated Gaussians were used in Ref. [32] to give an energy of positronium hydride of $-0.7892$ Hartree. Ref. [33] implemented a FCI and simultaneously optimized the centers and exponents of the Gaussian basis functions to find $-0.769$
Hartree for the ground state and $-0.676$ Hartree for the first excited state. Using configuration interaction with single-particle Gaussians Ref. [27] found an energy of $-0.7637$ Hartree. We have verified that our program can exactly recreate this result when using their basis set as detailed in Ref. [34]. A more accurate configuration interaction result was due to Ref. [35] which calculated the energy as $-0.7881$ eV using Laguerre polynomials as the single-particle basis functions and going to large angular momentum functions to achieve this result with 520990 configurations.

In Fig. 1 we display the calculated energy of positronium hydride as the MCCI calculation proceeds. Although the initial configuration has very high energy this is quickly reduced as the configuration space is expanded and the final result is lower in energy than a literature value [27] using single-particle Gaussians, but is not as accurate as a later result using Laguerre polynomials [35]. The latter result found a binding energy of 1 eV and we note that even an FCI with the aug-cc-pV5Z basis gives only 0.54 eV. Hence the difference is not a deficiency of the MCCI approach per se, but rather of the basis set. In fact, with a cutoff of $10^{-4}$ MCCI recovers 99.3% of the FCI binding energy but only uses 5.5% of the configurations, i.e., 3670 SDs compared with 67088. While a larger cutoff of $5 \times 10^{-4}$ needed just 1.9% of FCI the configurations, however only 94.1% of the FCI binding energy was recovered in this case.

![Figure 1: Configuration interaction (CI) results for positronium hydride with a line depicting the lowest energy that would not give a bound system. MCCI result uses $c_{\text{min}} = 5 \times 10^{-4}$ and the aug-cc-pV5Z basis. The result using single-particle Gaussians is from Ref. [27] and that using Laguerre polynomials is from Ref. [35].](image1)

We see that the MCCI results for the aug-cc-pVQZ and aug-cc-pV5Z basis give a bound state when varying the cutoff (Fig. 2) except for the largest $c_{\text{min}}$ considered ($5 \times 10^{-3}$) for the aug-cc-pV5Z basis. Interestingly the aug-cc-pVQZ result is lower than $-0.75$ Hartree at this cutoff despite only using 200 SDs and here we attribute the poorer performance of the MCCI aug-cc-pV5Z result to the five-times larger configuration space it is faced with. The error bars are only particularly noticeable for this calculation where the mean for ten runs is much lower than the energy from the wavefunction found in the first calculation, but remains higher than the aug-cc-pVQZ result.

![Figure 2: Positronium hydride energy calculated with MCCI using the aug-cc-pVQZ and aug-cc-pV5Z basis sets plotted against the cutoff ($c_{\text{min}}$). Standard errors around the mean from ten runs are also portrayed.](image2)

We quantify the multireference character of the wavefunction of the positronic system using the recently introduced measure $MR = \sum_i |c_i|^2 - |c|^4$ [36, 37]. Here a value of zero shows that the wavefunction consists of a single determinant when using the given molecular orbitals while MR tends to one as the number of important configurations increase. Table 1 shows that there is multireference character for these wavefunctions and we note that the dominant configuration has a coefficient of around 0.8. This multireference character is fairly robust against changes in the cutoff. However for the largest cutoff considered for aug-cc-pV5Z, the MR value is noticeably higher but even this value remains in the range 0.5 to 0.6. The noticeable difference in MR ties in with this particular calculation giving the only unbound result in Fig. 2. Table 1 also shows the possible benefit of using a doubly augmented basis to improve the radial description of the wavefunction. There the MCCI result at $5 \times 10^{-4}$ for d-aug-cc-pV5Z is lower in energy than the FCI result for aug-cc-pV5Z despite only using 2058 configurations compared with the FCI result requiring 67088.

![Table 1: MCCI energy (Hartree) and multireference character (MR) results with number of Slater determinants (SDs) for positronium hydride for a range of cutoff values ($c_{\text{min}}$) and basis sets.](image3)

<table>
<thead>
<tr>
<th>Basis</th>
<th>$c_{\text{min}}$</th>
<th>Energy</th>
<th>MR</th>
<th>SDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pV5Z</td>
<td>0</td>
<td>-0.77037642</td>
<td>0.54</td>
<td>67088</td>
</tr>
<tr>
<td>aug-cc-pV5Z</td>
<td>$10^{-4}$</td>
<td>-0.77022381</td>
<td>0.54</td>
<td>3670</td>
</tr>
<tr>
<td>aug-cc-pV5Z</td>
<td>$5 \times 10^{-4}$</td>
<td>-0.76917225</td>
<td>0.54</td>
<td>1250</td>
</tr>
<tr>
<td>aug-cc-pV5Z</td>
<td>$10^{-3}$</td>
<td>-0.76766505</td>
<td>0.54</td>
<td>782</td>
</tr>
<tr>
<td>aug-cc-pV5Z</td>
<td>$5 \times 10^{-3}$</td>
<td>-0.72704777</td>
<td>0.59</td>
<td>196</td>
</tr>
<tr>
<td>d-aug-cc-pV5Z</td>
<td>0</td>
<td>-0.77525677</td>
<td>0.58</td>
<td>150819</td>
</tr>
<tr>
<td>d-aug-cc-pV5Z</td>
<td>$5 \times 10^{-4}$</td>
<td>-0.77373357</td>
<td>0.57</td>
<td>2058</td>
</tr>
</tbody>
</table>

We also consider excited states when using the aug-cc-pV5Z basis. For the second state of $A_g$ symmetry in $D_{2h}$ we find an FCI value of $-0.607$ Hartree while the cutoff of
$5 \times 10^{-4}$ gives $-0.606$ Hartree using 2% of the configurations. Interestingly the multireference character, at 0.39, was lower than the ground-state. For the state of $B_{\text{min}}$ symmetry we find $-0.649$ Hartree for the FCI and $-0.648$ Hartree for $c_{\text{min}} = 5 \times 10^{-4}$. We note that this is higher in energy than the excited state result of Ref. [33] despite the aug-cc-pV5Z FCI ground-state being lower in energy than their corresponding result. In this case optimising the basis functions seems to offer greater advantages for excited state calculations than using a large quantum chemistry basis. We note that these excited states are not bound and the only known other stable state was calculated in Ref. [38].

### 3.2. Lithium

We next look at the stability of a lithium atom with a positron. A binding energy of $0.059$ eV was found in Ref. [39] using a stochastic procedure to optimize the correlation basis functions. The results of Ref. [32] using explicitly correlated Gaussians also suggested that the lithium atom could form a stable complex with a positron. An earlier work had found this system to be unstable [40] which was also the conclusion of a diffusion Monte Carlo study [41]. However a later diffusion Monte Carlo result [42] found the system to be stable with a binding energy of $0.065$ eV, then work by Mitroy [43] found a binding energy of $0.067$ eV using 1200 explicitly correlated Gaussians. Bromley and Mitroy [44] found that basis functions with angular momentum up to $l=29$ were necessary to calculate the system as bound when using configuration interaction with a semi-empirical polarization potential. Standard quantum chemistry basis sets are therefore likely to be insufficient to accurately model lithium with a positron.

When using the aug-cc-pV5Z basis with one frozen orbital we find that the FCI calculation used 2277 SDs while a cutoff of $5 \times 10^{-4}$ for MCCI resulted 441 SDs. Both calculations were lower in energy than the lithium atom by $0.79$ eV however they were higher in energy by $0.68$ eV when compared with dissociation into the cation and positronium. Absolute energies for this system, and subsequent systems considered, are available in the Supplementary Material.

### 3.3. Lithium positride

We also consider the lithium anion with a positron (lithium positride). The extra electron may be expected to be make this more stable than the atom with a positron. In Ref. [9] this stability was demonstrated when using stochastic optimization of explicitly correlated basis functions. There a binding energy of $0.33$ eV was calculated when using a fixed core approximation. We find that the FCI result for the aug-cc-pVQZ basis with one frozen orbital is lower in energy than the lithium anion by around $5.4$ eV however, again, it is not stable against dissociation into lithium and positronium. We see in table 2 that the MCCI result with $c_{\text{min}}=5 \times 10^{-4}$ is very close to that of FCI but uses only around 7% of the configurations. Similarly to positronium hydride we find that a doubly augmented basis with a reasonable cut-off can give a better result than the FCI value of the singly augmented basis, although not as good as moving to an aug-cc-pV5Z basis. The FCI result has reasonably strong multireference character of 0.78. The MCCI result with $c_{\text{min}}=5 \times 10^{-4}$ for the aug-cc-pV5Z basis is only slightly more computationally challenging than that with the smaller basis and results in an improvement in the binding energy but the system remains predicted to be unstable with these quantum chemistry basis sets.

#### Table 2: MCCI results for lithium positride with one frozen core orbital with the binding energy relative to lithium and positronium given in eV.

<table>
<thead>
<tr>
<th>Basis</th>
<th>$c_{\text{min}}$</th>
<th>Binding Energy</th>
<th>SDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVQZ</td>
<td>0.0005</td>
<td>$-0.71$</td>
<td>4628</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>0</td>
<td>$-0.68$</td>
<td>65180</td>
</tr>
<tr>
<td>d-aug-cc-pVQZ</td>
<td>0.0005</td>
<td>$-0.67$</td>
<td>6273</td>
</tr>
<tr>
<td>aug-cc-pV5Z</td>
<td>0.0005</td>
<td>$-0.52$</td>
<td>6063</td>
</tr>
</tbody>
</table>

### 3.4. Magnesium

Magnesium was found to able to bind with a positron in Ref. [12]. There around 200 orbitals with angular momentum quantum numbers up to $l = 12$ were used with FCI to give a binding energy of $0.43$ eV when using five frozen orbitals. In table 3 we see that MCCI with the aug-cc-pVQZ basis also gives the system as bound when using five frozen orbitals except at the lowest cutoff considered of $5 \times 10^{-3}$. However the aug-cc-pVQZ FCI result ($c_{\text{min}}=0$) of $0.14$ eV is around a third of the value of that of Ref. [12]. We note that the aug-cc-pVQZ basis consists of 84 orbitals which have up to $l=4$. The aug-cc-pVQZ FCI result required 925 SDs for Mg and 68559 for $e^+\text{Mg}$ while a cutoff of $10^{-4}$ gave 98% of the FCI binding energy, but used only 301 and 9748 determinants respectively, i.e., around 14% of the determinants needed for the FCI calculation of the positron containing system. The aug-cc-pVQZ FCI result for the positronic system had $\Delta R = 0.73$. We also find that by moving to a doubly augmented basis we can find a higher binding energy using just 3536 configurations than both the aug-cc-pVQZ FCI binding energy and the MCCI result in the single augmented basis that used 9748 configurations.

We next investigate the effect of the number of frozen orbital when using a cutoff of $10^{-4}$ with MCCI and the aug-cc-pVQZ basis set. We see in Fig. 3 that the positronic system is stable when the four or five lowest energy orbitals are frozen otherwise, however, the system is unbound. The increase in the number of SDs for the atom is much larger on going from five frozen orbitals to zero (301 to 8212) than for the positronic system (9748 to 10390). Although the energy of the electronic system is lowered substantially by
Table 3: Binding energy (eV) of \( e^+ \text{Mg} \) and number of Slater determinants (SDs) with variation of cutoff (\( c_{\text{min}} \)) for MCCI when using five frozen orbitals.

<table>
<thead>
<tr>
<th>Basis</th>
<th>( c_{\text{min}} )</th>
<th>Binding (eV)</th>
<th>SDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVQZ</td>
<td>0</td>
<td>0.141</td>
<td>68559</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>( 10^{-4} )</td>
<td>0.139</td>
<td>9748</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>( 5 \times 10^{-4} )</td>
<td>0.114</td>
<td>3011</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>( 10^{-3} )</td>
<td>0.084</td>
<td>1592</td>
</tr>
<tr>
<td>aug-cc-pVQZ</td>
<td>( 5 \times 10^{-3} )</td>
<td>-0.132</td>
<td>292</td>
</tr>
<tr>
<td>d-aug-cc-pVQZ</td>
<td>( 10^{-4} )</td>
<td>0.195</td>
<td>14372</td>
</tr>
<tr>
<td>d-aug-cc-pVQZ</td>
<td>( 5 \times 10^{-4} )</td>
<td>0.160</td>
<td>3536</td>
</tr>
<tr>
<td>d-aug-cc-pVQZ</td>
<td>( 10^{-3} )</td>
<td>-0.151</td>
<td>480</td>
</tr>
<tr>
<td>d-aug-cc-pVQZ</td>
<td>( 5 \times 10^{-3} )</td>
<td>-0.262</td>
<td>108</td>
</tr>
</tbody>
</table>

The table shows that freezing any orbitals the effect on the positronic system is much smaller. We see that the energies become higher on moving from one frozen orbital to zero in both cases. We attribute this to the configuration space increasing hence the problem becomes more challenging for MCCI with a reasonable cutoff. In addition the procedure will be less efficient in approaching an optimum wavefunction as new configurations formed by replacing what was a core orbital are unlikely to be necessary for the final wavefunction. We also suggest that this may be why the positronic system becomes unbound in that rather than spending enough time improving the positronic part of the wavefunction the current approach will be trying ineffective replacements of important electronic orbitals.

3.5. Lithium hydride

We now consider a molecule with a positron: lithium hydride. A positron affinity of around one electron volt was found in Ref. [45] using a variational calculation of explicitly correlated Gaussians. An earlier study [46] using configuration interaction with the 6-311G** basis set augmented with other Gaussian functions and one frozen orbital found an affinity of 0.46 eV. A multireference singles and doubles configuration interaction calculation (MRD-CI) [47] computed a value of 0.73 eV when using one frozen core with a bond length 3.05 Bohr without a positron and 3.30 Bohr with a positron. Variational quantum Monte Carlo gave a value of 0.47 eV in Ref. [10] followed by diffusion Monte Carlo to also find around 1 eV for the positron affinity. There a bond length of 3.015 Bohr was used for the molecule which became 3.348 Bohr when a positron was included. We use these geometries to investigate the positron affinity with MCCI. The aug-cc-pVQZ basis is employed and we freeze one molecular orbital. We note that the energy of the positronic system was higher with d-aug-cc-pVQZ than for aug-cc-pVQZ and the number of configurations was lower. This resulted in a negative positron affinity. We attribute this to the number of basis functions (167) being too challenging for the current version of the program to sample enough of the configuration space. In Table 4 we see that the MCCI results demonstrate the stability of the positronic system with respect to the molecule and are comparable to an MRD-CI calculation, but lower than values from diffusion Monte Carlo or correlated Gaussians. However the MCCI positron affinity is greater than an earlier configuration interaction calculation using single-particle Gaussians. The larger cutoff used for MCCI in the calculation of the positronic molecule resulted in a wavefunction comprising 7611 SDs while the smaller cutoff required 35093. The molecule needed 1395 and 2076 SDs respectively. For the cutoff of \( 10^{-4} \) the MCCI wavefunction for the molecule was dominated by a single SD (\( MR = 0.06 \)) while that of the positronic molecule was fairly strongly multireference with a value of 0.79.

Table 4: LiH positron affinities where the MCCI results use the aug-cc-pVQZ basis with one frozen orbital.

<table>
<thead>
<tr>
<th>Method</th>
<th>Positron affinity (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Configuration interaction</td>
<td>0.46</td>
</tr>
<tr>
<td>Correlated Gaussians</td>
<td>1.01</td>
</tr>
<tr>
<td>VMC [10]</td>
<td>0.47</td>
</tr>
<tr>
<td>FN-DMC [42]</td>
<td>0.87</td>
</tr>
<tr>
<td>FN-DMC [10]</td>
<td>1.01</td>
</tr>
<tr>
<td>MRD-CI [47]</td>
<td>0.73</td>
</tr>
<tr>
<td>MCCI (5 ( \times 10^{-4} ))</td>
<td>0.64</td>
</tr>
<tr>
<td>MCCI (10 ( \times 10^{-4} ))</td>
<td>0.78</td>
</tr>
</tbody>
</table>

3.6. Hydroxyl radical

We finally consider the hydroxyl radical with positronium (positronium hydroxide). The energy of this system should be compared against dissociation into OH and positronium to assess its stability using \( PA(OH^-) + \Delta E(A) = \Delta E(\text{positronium}) \). Hence the electron affinity of OH is also calculated. A binding energy of 0.7 eV using Møller-Plesset second-order perturbation and the 6-31G basis with diffuse functions was found in Ref. [48]. However it was noted [49] that this assumed an electron affinity for OH of
2.6 eV when the correct value should be around 1.8 eV. In this case the results do not suggest a bound state. A later diffusion quantum Monte Carlo study [50] calculated a hydroxide ion positron affinity of 5.57 ± 0.15 eV and the electron affinity of OH, in agreement with experiment, as 1.86 ± 0.14 eV resulting in 0.63 ± 0.15 eV for the binding energy.

We test MCCI on this system with a bond length of 0.965 Å and the aug-cc-pVDZ basis set which comprises 32 functions. In table 5 we see that at the largest cutoff considered the system is not bound and, similarly to Fig. 3, the results are affected by the number of frozen orbitals. With one frozen orbital, we can get within 0.7 eV of the diffusion quantum Monte Carlo result by lowering the cutoff to 10⁻⁴, however the electron affinity of OH is calculated as 1.57 eV at this level to give a binding energy of −0.35 eV. With three frozen orbitals the electron affinity of OH is 1.82 eV resulting in the system being bound but with the low value of 0.08 eV. The largest cutoff result is significantly improved by moving to the d-aug-cc-pVDZ basis which has 45 functions, but the system is still not bound. With three frozen orbitals the binding energy is now 0.30 eV when more radial basis functions are included.

<table>
<thead>
<tr>
<th>Basis</th>
<th>c_min</th>
<th>FO</th>
<th>PA (eV)</th>
<th>SDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>aug-cc-pVDZ</td>
<td>5 × 10⁻⁴</td>
<td>1</td>
<td>2.25</td>
<td>5245</td>
</tr>
<tr>
<td>aug-cc-pVDZ</td>
<td>10⁻⁴</td>
<td>1</td>
<td>4.89</td>
<td>81311</td>
</tr>
<tr>
<td>aug-cc-pVDZ+Ry</td>
<td>10⁻⁴</td>
<td>3</td>
<td>5.07</td>
<td>17571</td>
</tr>
<tr>
<td>d-aug-cc-pVDZ</td>
<td>5 × 10⁻⁴</td>
<td>1</td>
<td>4.76</td>
<td>17150</td>
</tr>
<tr>
<td>d-aug-cc-pVDZ</td>
<td>10⁻⁴</td>
<td>1</td>
<td>5.15</td>
<td>113781</td>
</tr>
<tr>
<td>d-aug-cc-pVDZ</td>
<td>10⁻⁴</td>
<td>3</td>
<td>5.27</td>
<td>36627</td>
</tr>
</tbody>
</table>

We also further augment the aug-cc-pVDZ basis with Rydberg functions centered on oxygen (see Supplementary Material) to give a total of 107 basis functions. With a cutoff of 10⁻⁴ and 3 frozen orbitals we find that 49633 SDs were required to give a positron affinity of 5.43 eV. Using this approach we find an electron affinity of 1.86 eV and, therefore, a binding energy of 0.49 eV.

4. Summary

We have adapted the approach of Monte Carlo configuration interaction (MCCI) to calculate the energy of positron system using quantum chemistry basis sets. We saw that positronium hydride could be correctly predicted to be bound using this method and, with the aug-cc-pV5Z basis, we were able to recover 99.3% of the full configuration interaction (FCI) binding energy but only using 5.5% of the configurations. This result required around 6 minutes compared with the 242 minutes needed for our FCI (c_min=0) calculation to demonstrate convergence when running on 12 processors. However when using quantum chemistry basis sets our most accurate binding results (d-aug-cc-pV5Z) reached around 70% of the most accurate literature value that used a Laguerre basis and included orbitals with high angular momentum.

We then turned to lithium with a positron and found that, although lower in energy than the lithium atom, this method suggested an unstable system with respect to the cation and positronium. We attributed this to the very small binding energy being too challenging for this stochastic approach with the basis sets employed.

When using the same number of frozen core orbitals as the literature we found that magnesium would stably bind to a positron for all except the largest MCCI cutoffs considered when using the aug-cc-pVQZ basis. However even the FCI result in this basis was around a third of the literature value. By improving the radial description of the wavefunction through using the d-aug-cc-pVQZ basis we were then able to use fewer configurations to capture about 45% of the literature result when using an MCCI cut off of 10⁻⁴. We also saw for this system that the number of frozen core orbitals strongly affected whether an MCCI calculation gave the system to be bound.

We found a positron affinity for lithium hydride using MCCI that was the correct order of magnitude and larger than some literature values but lower than work using correlated Gaussians or diffusion Monte Carlo.

Finally we looked at positronium hydroxide. The MCCI results showed that the hydroxide ion was lowered in energy on capturing a positron. We saw that again the results were dependent on the number of frozen core orbitals. With the aug-cc-pVQZ basis we had to freeze three orbitals to find that positronium hydroxide was weakly bound with respect to dissociation into OH and positronium. While added Rydberg functions were necessary, and a relatively large number of SDs (49644), to find a result closer to the literature value.

We have shown that MCCI can be adapted to tackle positronic molecules and that a small fraction of the determinants necessary for an FCI can capture much of the FCI energy of the positronic system. However the percentage required was not as small as has been observed [20, 21, 22, 21, 23] when MCCI is applied to electronic systems which we attribute to the relatively large multireference character of the FCI positronic wavefunctions in this work. With quantum chemistry basis sets we found that we could calculate qualitative positron affinities and results for lithium hydride were more accurate than previous configuration interaction results. However the small binding energies for lithium with a positron were too challenging. The method did correctly determine that magnesium and the hydroxide ion could stably bind with a positron, and we noted how the number of frozen orbitals could affect the results. The relatively large multireference character of the positronic wavefunctions supported the acknowledged difficulty in modelling these systems us-
The compact wavefunctions produced by MCCI could be used as a starting point in the optimization of single-particle basis sets for the description of positronic systems and perhaps the natural orbitals calculated from these wavefunctions might be investigated as possible basis functions. MCCI results for atomic ionization energies were extrapolated to the complete basis set limit in Ref. [23] and it would be interesting to see if MCCI positronic results can be estimated in an analogous manner perhaps by adapting the approaches of Ref. [35].

Acknowledgments

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References

Figure

- Energy (Hartree)
- Iteration

- MCCI 0.0005 aug-cc-pV5Z
- CI single-particle Gaussians
- CI Laguerre polynomials
- Unbound System
Frozen Orbitals

Energy (Hartree)

-199.675
-199.67
-199.665
-199.66
-199.655
-199.65

Mg

Mg with positron

Figure