Comment on "Multireference configuration-interaction calculations for positronium halides" [J. Chem. Phys. 122, 054302 (2005)]

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In a recent series of papers Saito[1–3] performed large configuration–interaction (CI) calculations on the PsH, PsF, PsCl, PsBr, and PsI exotic atoms. In the most recent article, he estimates the two-photon annihilation rates Γ were 2.02×10^9 s^{-1} for PsF, 1.50×10^9 s^{-1} for PsCl, 1.37×10^9 s^{-1} for PsBr, and 1.25×10^9 s^{-1} for PsI.[3] Since three of these systems have annihilation rates smaller than the spin-averaged Ps annihilation rate of $\approx2.01\times10^9$ s^{-1}, they concluded that the ground state of the positronium halide has a diatomic molecular structure structure, PsX, and its Ps broadens from PsF to PsI. It may be that positronium halides with broad Ps have a large component of atomic structure e^+-X^-. The Saito calculations are not large enough to make this conclusion with any degree of certainty and furthermore, the idea that there has been significant broadening of the Ps cluster is at variance with experience gained on other positron binding complexes.

First, there are four Ps binding systems, PsH, LiPs, NaPs, and KPs, with close to converged wave functions since they were obtained with correlated basis sets. All of these systems give a Γ larger than that of neutral Ps. The best explicitly correlated Gaussian basis sets give 2.47×10^9 s^{-1} for PsH, 2.16×10^9 s^{-1} for LiPs, 2.11×10^9 s^{-1} for NaPs, and 2.07×10^9 s^{-1} for KPs (note that these Γ are obtained with better wave functions than those given previously[4]).

Arguments based on second-order perturbation theory[5] suggest that the partial-wave increments to Γ should scale as $\Delta\Gamma_\ell=a\ell^{-p}$, where $p=2$ and ℓ is the orbital angular momentum of the largest ℓ orbital under consideration. All the bound-state and scattering calculations reported in Refs. 6–10 are consistent with this result. Typically, it is found that $p\approx1.8$ at $\ell=10$, but with the variation of p with ℓ suggestive of the expected limit of $p=2$. However, the functional form used by Saito, $\Delta\Gamma_\ell=10^{-a(\log\ell)^b+c}$, is not based on any physical principles. It is evident from Fig. 4 of Saito[3] that the extrapolated increments $\Delta\Gamma_\ell$ are decreasing much faster than ℓ^{-2} for $\ell>8$. When Saito applies this extrapolation to PsH, it increases their explicitly calculated Γ from 1.780×10^9 s^{-1} to $\Gamma=2.07\times10^9$ s^{-1}, while the actual contribution from the higher ℓ values should be about twice as large.[6]

The number of natural orbitals (NOs) used by Saito is different for electrons and positrons at $\ell=8$. It has been found *in all* our calculations[6–10] that the optimized Laguerre-type orbital (LTO) basis sets used to represent the positron and electron orbitals become identical as ℓ increases. The high-ℓ orbitals needed in mixed electron–positron systems arise due to the tendency of the electron and positron to coalesce into something that resembles the Ps ground state. At high ℓ the dominant interaction for both the electrons and positron is the $\ell(\ell+1)/(2r^2)$ centrifugal interaction. So the optimized high-ℓ electron and positron single-particle orbitals should be the same. Therefore it is extremely worrisome that the PsF Saito NO list has six e^- and only four e^+ NOs at $\ell=8$. For small values of ℓ, one does expect the electron and positron orbitals to be different, and this has been noticed in CI calculations of positron binding to heavier systems.[7,8] However, the optimal electron and positron basis sets are typically almost the same for $\ell\geqslant3$. Since, the asymptotic large r form of the PsX (X=halogen atom) wave function is Ps$(1s)+X(^2P^0)$, one does expect the e^-/e^+ basis sets to be similar at $\ell=8$.

The number of positron NOs at high ℓ is also small, with only four or five positron NOs for $\ell\geqslant5$. Experience with CI calculations using a LTO basis suggests that calculations of this size are likely to significantly underestimate the increments to the Γ. One can compare the incremental annihilation rates of some small basis calculations[11] with those using a larger basis.[6] For example, $\Delta\Gamma_7=0.0422\times10^9$ s^{-1} for a PsH calculation with five radial functions, while $\Delta\Gamma_7=0.0672\times10^9$ s^{-1} for a calculation with eight radial functions.[6]

It should be noted that the NO basis does not show any major superiority to the LTO basis. Our largest explicit CI-LTO calculation for PsH with 91 (90) electron (positron) orbitals up to $\ell_{\max}=9$ gave a binding energy of $-0.786\,776$ hartree and a $\Gamma=1.791\times10^9$ s^{-1}. The CI-NO calculation of Saito[1] gave $-0.786\,793$ hartree and $\Gamma=1.780\times10^9$ s^{-1}. We have since performed even larger calculations; a CI-LTO calculation with 153 electron/positron orbitals gave $-0.787\,006$ hartree and $\Gamma=1.842\times10^9$ s^{-1}.

One feature that we noted during our calculations, but did not make explicit mention about, was the sensitivity of the Γ_ℓ to the size of the radial basis. For example, the 90 (91) orbital calculation gives $p=1.76$ at $\ell=9$ assuming $a\ell^{-p}$ scaling. The larger 153 electron/positron calculation gives $p=1.61$. Once again, that p (at a given ℓ) has decreased as the radial basis is enlarged is something that we have noticed in *all* our calculations. Although the incremental changes to Γ get succesively smaller as ℓ increases, care needs to be taken, otherwise small calculations (such as the Saito calculations with only four or five positron NOs for $\ell>5$) could easily overestimate the rate at which the $\Delta\Gamma_\ell$ is decreasing.

The incremental, single-ℓ-at-a-time approach used by Saito to generate the NOs may be acceptable for purely electronic states, but is fraught with peril when calculating the Γ for mixed electron-positron systems. Saito generates the NO basis in a piecemeal approach and uses a fixed ℓ-independent energy tolerance to decide whether to include a NO or not. Since the energy increments with ℓ decrease much faster (second-order perturbation theory[5] predicts ℓ^{-4}, although we have found $\sim\ell^{-3}$ for most systems at $\ell=10$) than the $\Delta\Gamma_l$, it is possible that this could result in an artificially accelerated convergence rate for Γ. To successfully extrapolate the contributions from the highest ℓ terms does require that the individual terms be calculated with the same *relative* accuracy and this can scarcely be done with a fixed energy-based selection criteria. It is probably not a coincidence that the Saito calculation with the tightest NO truncation threshold, i.e., PsF, also had the largest Γ.

The speed of the convergence of the partial-wave series depends on the radial distance from the nucleus where electron–positron localization is strongest. Generally, the further this occurs from the nucleus, the slower the convergence. So convergence for Ps binding systems should be slower for systems where the mean positron distance is farther from the nucleus. Unfortunately, Saito does not report any radial expectation values, but one can reasonably infer from the binding energies that PsI is more loosely bound than PsF. However, the number of positron NOs for PsF and PsI are roughly the same. So the possibility of the Saito calculation increasingly underestimating Γ as the PsX binding energy decreases should be regarded as likely.

Another potential problem with incremental basis optimization is that the radial NO basis with say $\ell=2$ generated from a small calculation with $\ell_{\max}=3$ may not be the best basis for a much larger calculation with $\ell_{\max}=8$. While doing our CI calculations[6–8] we found that the radial basis for a given ℓ could be different if it was optimized in CI calculations with substantially different values of $\ell_{\max}$. When generating something akin to a Ps cluster from an expansion with ten ℓ values and up to 100 orbitals, it is desirable that all these strongly coupled orbitals be optimized simultaneously.

The limitations of the Saito approach are also evident in their Γ calculation of the PsH state with the two electrons in a spin-triplet state.[1] This state is not bound, and Saito has effectively diagonalized the electron–triplet PsH hamiltonian in a box of radius $40a_0$ (the outmost point of their B-spline radius). Such a system will evolve into separate Ps$(1s)$ + H$(1s)$ systems, with their spatial separation determined by the size of the box. Therefore one expects such a calculation to yield $\Gamma\approx 2.0\times 10^9$ s^{-1}. Saito obtains $\Gamma=1.08\times 10^9$ s^{-1} when using the same methodolgy as their Ps-halide calculations; a gross underestimate. This is further reinforced by some calculations of PsH scattering[12,13] undertaken by one of us (J.M.). A preliminary step in these calculations was the generation of a series of wave functions (using an explicitly correlated basis set) for the PsH electron–triplet state in what is effectively a "soft-sided" box. Irrespective of the effective radius, these wave functions give Γ in the range $1.90-1.96\times 10^9$ s^{-1}.

To summarize, the singular feature that differentiates mixed electron–positron CI calculations from purely electron CI calculations is the slow convergence with respect to ℓ, which manifests itself most severely in the evaluation of Γ. The annihilation-rate-driven conclusions of Saito about the structure of Ps–halide systems are likely to be proven erroneous due to the misplaced optimism of the author in the approach used to generate the natural orbitals and the extrapolation procedure used to estimate the $\ell\rightarrow\infty$ limit. One should not conclude that Γ for any PsX system (where X is a neutral atom) is smaller than that of the Ps ground state until proven by a series of exhaustive calculations, and this is not the case for the Saito calculation.[3]

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