Comment on "Cavity Induced Shift and Narrowing of the Positronium Lyman-α Transition"

In a recent Letter [1] Cassidy *et al.* reported an observation of a shift of the $1s$-$2p$ transition energy for positronium (Ps) inside a porous silica film, relative to the corresponding transition in vacuum. They also calculated this "cavity shift" for Ps in a spherical Woods-Saxon-type confining potential as a function of the cavity size using a configuration interaction (CI) method, and found that it "decreases dramatically for larger cavity diameters" with a "sharp change in slope at ~5 nm diameter." These findings, however, contradict the estimate made by Cassidy *et al.* in their Letter, and we believe that this behavior is an artifact of the calculation.

Typical pore diameters in the sample, $d \sim 5$ nm [1], are much greater than the mean radius r_{nl} of the Ps atom in either the ground or excited state nl. Ps atoms interact with the cavity when they are close to the walls. This results in a $1/d^3$ dependence of the cavity shift (see below). The Ps-cavity problem does not contain any other length scales besides r_{nl} and d. There is therefore no physical reason for a sharp change in the cavity shift for any particular value of $d \gg r_{nl}$.

The wave function of Ps in the ground state of the center-of-mass (c.m.) motion inside a spherical cavity is $\Psi_{nl}(\mathbf{R}, \mathbf{r}) = AR^{-1} \sin kR \varphi_{nl}(\mathbf{r})$, where $\mathbf{R}$ is the Ps c.m., k is the corresponding wave number, A is the normalization constant, and φ_{nl} is the Ps internal state. For the c.m. motion confined by a hard-wall cavity of radius $R_0 = d/2$, the condition $kR_0 = \pi$ gives the total Ps energy (in atomic units) $E_{nl} = k^2/2M + \varepsilon_{nl} = \pi^2/2MR_0^2 + \varepsilon_{nl}$, where M is the Ps mass and ε_{nl} is its internal energy. In this picture the cavity shift $\delta\varepsilon$ is due to the different *effective* radii of the cavity for the Ps in the $1s$ and $2p$ states, $R_{nl} = R_0 - \delta_{nl}$. For $\delta_{nl} \ll R_0$ this gives $\delta\varepsilon \simeq \pi^2(\delta_{2p} - \delta_{1s})/MR_0^3$, which shows that $\delta\varepsilon \propto d^{-3}$. If the effective reduction of the cavity size is determined by the mean radius of the Ps atom, $\delta_{nl} \sim r_{nl} = 3n^2 - l(l+1)$, the $1s$-$2p$ shift is $\delta\varepsilon \sim 7\pi^2/MR_0^3$. This estimate is in agreement with that made by Cassidy *et al.* [1], except that they used a smaller value of $\delta_{2p} - \delta_{1s} = 3$ a.u.

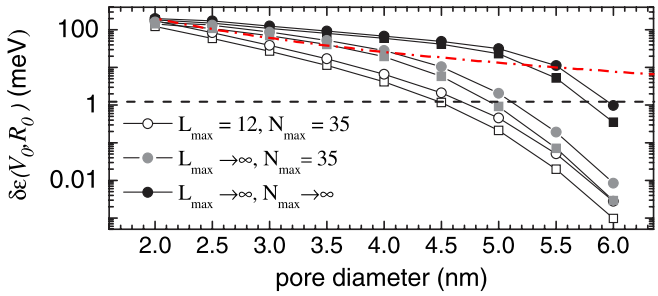

FIG. 1 (color online). Various symbols show the calculated cavity shift from Cassidy *et al.* [1]. The chain curve shows $1/d^3$ dependence with $\delta\varepsilon$ set to the CI result at the pore diameter of 2 nm.

Alternatively, we can estimate the perturbative shift of the c.m. energy due to the Ps interaction with the cavity wall $V_{nl}(R)$, $\Delta E_{nl} = 4\pi A^2 \int_0^{R_0} \sin^2 kR V_{nl}(R) dR$. Assuming that $V_{nl}(R)$ is confined to a thin shell of thickness $\xi \sim r_{nl} \ll R_0$, one obtains $\Delta E_{nl} \sim 2\pi^2 \bar{V}_{nl} \xi^3 / R_0^3$, where $\bar{V}_{nl}$ is the typical strength of the potential. This gives the cavity shift $\delta\varepsilon \sim 2\pi^2(\bar{V}_{2p} - \bar{V}_{1s})\xi^3/R_0^3$, which is again inversely proportional to d^3.

In contrast, the behavior of the cavity shift calculated in Ref. [1] exhibits an unphysical rapid drop when the Woods-Saxon cavity diameter exceeds $d \sim 5$ nm (see Fig. 1). Such behavior must be an artifact of the numerical calculation. The CI expansion contains a limited number $N_{\max}$ of Laguerre-type radial orbitals with exponential factors $e^{-\lambda r}$. This introduces an artificial confinement with an effective radius R_λ. It is probably exacerbated by the insufficient number of electron and positron partial waves. To describe Ps far from the origin, a single- center CI expansion must include high angular momenta $L_{\max} \gtrsim R_0/r_{nl}$. For smaller $L_{\max}$ the CI wave function does not resolve small electron-positron separations, which increases the energy of the system. Extrapolating $N_{\max} \to \infty$ and $L_{\max} \to \infty$ mitigates these problems, but cannot overcome them completely. As a result, the CI calculation produces meaningful results for cavity sizes of $R_0 < R_\lambda \sim 4$ nm, while for $R_0 > R_\lambda$ the effect of the Woods-Saxon potential rapidly diminishes, leading to a sharp drop of the cavity shift.

Another feature of the calculation that has no sound physical explanation is the large difference between the mean electron and positron radii in the $1s$ and $2p$ Ps-cavity states: $\langle r_e \rangle = \langle r_p \rangle \approx 7$ a.u. and $\langle r_e \rangle = \langle r_p \rangle \approx 17$ a.u., respectively, for $R_0 = 38$ a.u. [1]. The expectation value for the Ps c.m. ground state in the cavity is $\langle R \rangle = R_0/2 = 19$ a.u. Attributing the difference between the mean radii to the possibility of the $2p$ state to "tunnel into the barrier" [1] implies strong mixing between the internal and c.m. motion of Ps in the cavity. Such mixing is unlikely, given the very different energy scales of the two motions. It is possible that the CI calculation describes the more diffuse Ps $2p$ state better than the $1s$ state, hence providing more consistent values of $\langle r_e \rangle$ and $\langle r_p \rangle$ for the former.

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