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NOTE

Cross section for photoionization of the positronium negative ion at the lowest Feshbach resonance

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Abstract: The photoionization cross section for the positronium (Ps) negative ion, Ps^-, at the lowest $n = 2$ Feshbach resonance, estimated by neglecting the influences of the weakly bound outer electron, is $\sigma_F = 1.4 \times 10^{-12}$ cm², about 3×10^3 times the existing lower limit calculated by Igarashi and co-workers (*New J. Phys.* **2**, 17 (2000)). Although the estimated cross section is 200 times smaller than the analogous cross section for photoexcitation of the Ps Lyman-α transition, including the effect of the broad line width of the resonance shows it will be feasible to observe this resonance to obtain precision information about the three body Ps^- system.

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Résumé : La section efficace de photo-ionisation de l'ion négatif Ps^- du positronium (Ps) à la plus basse résonance de Feshbach ($n = 2$), estimée en négligeant l'influence de l'électron extérieur faiblement lié, est $\sigma_F = 1.4 \times 10^{-12}$ cm², environ 3×10^3 fois la valeur de la limite inférieure calculée par Igarashi et al. (*New J. Phys.* **2**, 17 (2000)). Même si la section efficace estimée est 200 fois plus petite que la section efficace analogue pour la photo-excitation de la transition Lyman α du Ps, la prise en compte de l'effet de la large raie de la résonance montre qu'il sera possible d'observer cette résonance pour obtenir de l'information précise sur le système à trois corps Ps^-. [Traduit par la Rédaction]

Introduction

The positronium (Ps) negative ion (Ps^-) [1, 2] is a bound state of a positron and two electrons that can be formed efficiently with very low kinetic energies following positron implantation into a tungsten surface covered with a monolayer of alkali metal atoms [3–5]. It has thus recently become possible to observe the photodetachment of Ps^- [6–8] and possibly to make other optical measurements. Although Ps^- has no particle-stable excited states [9, 10], the existence of narrow Feshbach resonances just below the 2P threshold [11] suggests that spectroscopic measurements could yield valuable information about the Ps^- wave function and the radiative corrections to its energy structure [12]. Unfortunately the photoionization cross section of the lowest energy singlet resonance that would be most suitable for study is presently known only as a lower limit, 4×10^{-16} cm² [13, 14] because the calculated cross section of ref. 13 was not reported exactly on the resonance. While the nearly divergent behaviour of the cross section near the resonance [13] clearly indicates that the maximum value is much greater than the largest value calculated, the existing lower limit is so small that the experiment would not appear possible. In this note, a simple model is used to show that the cross section is about 3×10^3 times greater than the lower limit and that the resonance should be observable by optical excitation.

The lowest energy Feshbach resonance is reached from the Ps^- ground state via absorption of an ultraviolet photon indicated by dashed arrow 1 in the level diagram of Fig. 1. The resonance wavelength is 229.1351 nm not including radiative corrections (~–0.01 nm) and the width of the resonance is $\Gamma = (0.9 \pm 0.09) \times 10^{-6}$ a.u. [13, 15]. This corresponds to a full width at half maximum (fwhm) of the resonance frequency $\Gamma/h = (6.5 \pm 0.7)$ GHz and a mean lifetime of the resonance $\tau_F = \hbar/\Gamma = (24.4 \pm 2.4)$ ps. The lifetime is much shorter than the 3.2 ns mean lifetime of the 2P state of Ps by Lyman-α emission because the Ps^- Feshbach resonance decays principally by rapid Auger de-excitation of the level to ground state Ps plus a free electron, as indicated by the dashed arrows 2 in Fig. 1. Three-quarters of the Ps atoms thus produced would be in the triplet state, which could be detected either by its long lifetime or by its resonant Lyman-α (1S–2P) excitation [16].

Model and results

A simplified picture of the Ps^- ion (which has an annihilation mean lifetime $\tau_{Ps^-} = (479 \pm 3)$ ps [17]) is a ground state Ps atom surrounded by a weakly bound electron in a singlet state relative to the Ps electron, the binding energy being $E_{Ps^-} = 0.326\,67\ldots$ eV [18]. The resonant photoionization $h\nu + Ps^- \rightarrow e^- + Ps$ occurs as a first approximation by resonant photoexcitation of the perturbed 1S ground state of Ps approximating the "core" of the Ps^- system to a perturbed 2P Ps excited state. This is followed after a mean time $\tau_F \approx 24$ ps by Auger de-excitation of the resonance to a ground state Ps atom plus a free electron with release of total kinetic energy 5.084 eV, slightly less than the 5.102 eV Lyman-α energy, and corresponding to a Feshbach resonance binding energy relative to the Ps $n = 2$ state $E_F = 0.018$ eV. Less than 1% of the de-excitations will involve emission of a ~5 eV photon and a few meV electron.

The cross section for 1S–2P photoexcitation of Ps, defined as the ratio of the probability of excitation per 2P mean lifetime interval divided by the photon flux, is [19]

$$\sigma_{L\alpha} = 8\pi\alpha\, p_{L\alpha}^2 \omega_{L\alpha} \tau_{L\alpha} = \frac{2^7 \pi a_0^2}{3\alpha^2} = 2.81 \times 10^{-10}\ \text{cm}^2 \tag{1}$$

where the transition dipole moment [20] is $p_{L\alpha} \equiv \langle 2P|z|1S\rangle = 4\sqrt{2}(2/3)^5 a_0$, $a_0 = 2a_B$ is the Ps Bohr radius, $\omega_{L\alpha} = 3\alpha c/8a_0$ is the

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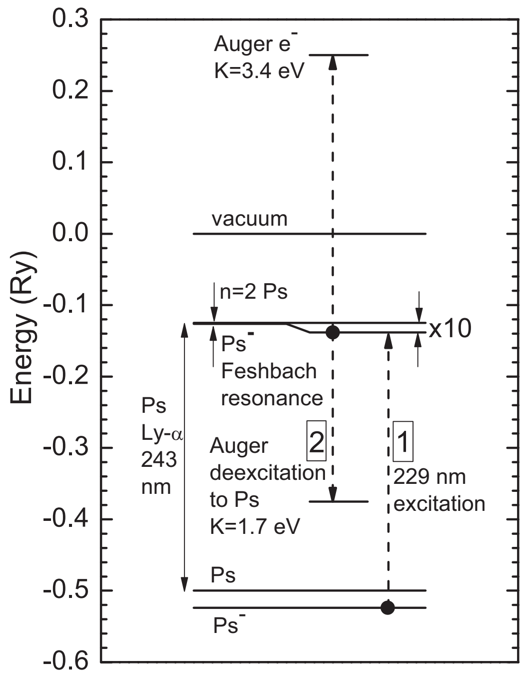
Fig. 1. Partial level diagram of Ps and Ps⁻ showing the pathways for (arrow 1) excitation of Ps⁻ to the lowest energy Feshbach resonance, and (arrow 2) Auger de-excitation of this state to a free ground state Ps atom with kinetic energy $K = 1.7$ eV and a free electron with $K = 3.4$ eV in the center of mass reference frame of the original Ps⁻.



angular frequency of the Lyman-α transition, $\alpha \equiv e^2/\hbar c = 1/137.036\ldots$ [cgs units] is the fine structure constant, and $\tau_{L\alpha} = 3^8 2^{-8} \alpha^{-4} a_0 c^{-1} = 3.18$ ns is the mean lifetime of the 2P state of Ps. This is to be compared with the analogously defined cross section for photoexcitation of the $n = 2$ Feshbach resonance

$$\sigma_F = 8\pi\alpha p_F^2 \omega_F \tau_F = \sigma_{L\alpha} \frac{p_F^2 \omega_F \tau_F}{p_{L\alpha}^2 \omega_{L\alpha} \tau_{L\alpha}} \tag{2}$$

In our simple approximation the transition dipole moment is

$$p_F \equiv \langle 2P|z|1S\rangle \langle \phi_{Ps-}|\phi_F\rangle = p_{L\alpha} \langle \phi_{Ps-}|\phi_F\rangle \tag{3}$$

where $\langle \phi_{Ps-}|\phi_F\rangle$ is the overlap between the spectator electron wave functions in the Ps⁻ ground state and the Feshbach resonance.

To the extent that the spectator electron is experiencing a short-range isotropic attractive potential (see Appendix A), its wave function in the two states will have the same mathematical form for large radial separations, r, as a deuteron wave function, namely

$$\phi(r) = \sqrt{\frac{2\mu}{4\pi}} \frac{e^{-\mu r}}{r} \tag{4}$$

Because $\nabla^2 \phi(r) = \mu^2 \phi(r)$, the inverse length, μ, is given in terms of the binding energy, E_s of the spectator electron state by $\mu = \sqrt{2 m_r E_s/\hbar^2}$, where $m_r = (2/3) m_e$ is the reduced mass of the spectator electron. The overlap inner product in the approximation to the dipole moment in (3) then becomes

$$\langle \phi_{Ps^-}|\phi_F\rangle = \frac{2}{4\pi}\sqrt{\mu_{Ps^-}\mu_F} \int_0^\infty \frac{e^{-(\mu_{Ps^-}+\mu_F)r}}{r^2} 4\pi r^2 dr = \frac{2\sqrt{\mu_{Ps^-}\mu_F}}{\mu_{Ps^-} + \mu_F} \tag{5}$$

where the inverse lengths μ_{Ps^-} and μ_F are to be evaluated using the binding energies of Ps⁻ ($E_{Ps^-} = 0.326$ eV) and the lowest energy Feshbach resonance relative to the 2p threshold ($E_F = 0.018$ eV). The square of the overlap is then

$$|\langle \phi_-|\phi_F\rangle|^2 = \frac{4\mu_{Ps^-}\mu_F}{(\mu_{Ps^-} + \mu_F)^2} = \frac{4\sqrt{E_{Ps^-}E_F}}{\left(\sqrt{E_{Ps^-}} + \sqrt{E_F}\right)^2} = 0.616 \tag{6}$$

from which we obtain, using (1)–(3)

$$\sigma_F = 1.4 \times 10^{-12}\ \mathrm{cm}^2 \tag{7}$$

Reference 13 gives the oscillator strength sum for all the Feshbach resonances below the $n = 2$ Ps threshold as $O = 0.69$ of the total oscillator strength summed over all optical transitions from the Ps⁻ ground state. In terms of the oscillator strength, the cross section would be [19]

$$\sigma_F = O \times 2\pi \left(\frac{m_e}{m_r}\right) r_0 c \tau_F = \left(\frac{m_e}{m_r}\right) \times 0.69 \times 1.3 \times 10^{-12}\ \mathrm{cm}^2 \tag{8}$$

This expression is strictly only valid for a single electron atom, but it agrees with (7) if we use a reduced mass appropriate for the Ps⁻ ion, $m_r = (2/3) m_e$, where m_e is the electron mass. Parenthetically, we note that the lowest energy Feshbach resonance cross section for H⁻ peaks at 1.43×10^{-15} cm² according to a calculation by Broad and Reinhardt [21, 22] using a small basis set, while a measurement by Bryant et al. [23] shows that the product of the peak measured cross section times the instrumental resonance full width at half maximum is about 2.0×10^{-20} cm² a.u. Dividing by the resonance width 10^{-6} a.u. [24] suggests that the maximum cross section might be about 2.0×10^{-14} cm² for H⁻, considerably smaller than the estimated Ps⁻ cross section.

Discussion

The numerical value of the $n = 2$ Ps⁻ Feshbach resonance cross section in (5) is about 3×10^3 times larger than the lower limit of ref. 13. On the other hand, it is only about 0.5% of the Ps Lyman-α absorption cross section, making it appear at first sight that one would require about 200 times more light intensity to observe the Ps⁻ Feshbach resonance. However, in an experiment [25] one must take into account the large Doppler widths of the Ps atom and Ps⁻ ion ensembles, and also the time structure and spectrum of the laser pulses.

Because the laser pulses may be longer than the time relevant to the definition of the cross section, we would like to know the expected yield, Y, of photoelectrons per Ps⁻ ion under illumination that lasts longer than the Ps⁻ lifetime. If we are coupling a ground state $|1\rangle$ to an excited state $|2\rangle$ via a perturbation $ezE_0\cos\omega t$, which gets turned on at time $t = 0$, the amplitude, $c_2(t)$, for the system being in the excited state, in the rotating frame approximation (which neglects the effect of rotation at frequencies ≈ 2ω) is expressed in the interaction picture as

$$\dot{c}_2(t) = \frac{1}{2i\hbar} e p E_0 \exp[i(\omega_{21} - \omega)t] c_1(t) \tag{9}$$

where the difference of the eigenvalues is $\omega_{21} = (E_2 - E_1)/\hbar = \omega_2 - (1/2)i/\tau_2 - \omega_1 + (1/2)i/\tau_1$. Assuming the amplitude for being in the ground state is slowly decaying as $c_1(t) \approx \exp\{-(1/2)\gamma_{Ps^-}t\}$ and $\tau_2 \ll \tau_1$, then exactly on resonance, when $\omega = \omega_2 - \omega_1$

$$c_2(t) = -2i\Omega\tau_2\left\{1 - \exp\left[-\left(\frac{1}{2}\right)\frac{t}{\tau_2}\right]\right\}\exp\left[-\left(\frac{1}{2}\right)\frac{t}{\tau_1}\right] \tag{10}$$

Here $\Omega \equiv eE_0p/2\hbar$ is the Rabi frequency and the equation is only valid for $4\Omega^2\tau_1\tau_2 \ll 1$. The total probability of there eventually being a decay event from state 2 is then

$$Y \approx \int_0^\infty |c_2(t)|^2 dt = 4\Omega^2\tau_1\tau_2 \tag{11}$$

This is the expected yield of photoelectrons when Ps^- is illuminated exactly at the Feshbach resonance for a time much longer than the Ps^- mean lifetime assuming $4\Omega^2\tau_1\tau_2 \ll 1$.

The analogous expression for the yield of 2P Ps for Ps that has been illuminated for a mean time t_{Laser} such that $t_{L\alpha} \ll t_{Laser} \ll \tau_{Ps(1S)}$ exactly on resonance is

$$Y_{L\alpha} \approx 4\Omega^2 t_{Laser}\tau_{L\alpha} \tag{12}$$

For $t_{Laser} = \tau_{L\alpha}$ we would have roughly 50% yield for $4\Omega^2\tau_{L\alpha}^2 = \hbar^{-2}e^2E_0^2p^2\tau_{L\alpha}^2 \approx 1$. This means the laser fluence required for exciting the Ps 1S to 2P Lyman-α resonance with ~50% probability (under conditions of zero Doppler broadening) would be [cgs units]

$$F_{L\alpha} = \frac{E_0^2 c\tau_{L\alpha}}{8\pi} = \frac{\hbar/\tau_{L\alpha}}{8\pi\alpha\, 2^{17}3^{-10}a_B^2} \approx 2.9\ \text{nJ/cm}^2 \tag{13}$$

The corresponding laser fluence required for exciting the Ps^- Feshbach resonance with ~50% probability would be

$$F_F = F_{L\alpha}\left(\frac{p_{L\alpha}}{p_F}\right)^2 \frac{\tau_{L\alpha}^2}{\tau_{Ps^-}\tau_F} \approx 1.5\ \mu\text{J/cm}^2 \tag{14}$$

Assuming the laser pulse does not have optimal width, which would be τ_{Ps^-}, but is rather equal to $\tau_{L\alpha}$, the required laser fluence for exciting the Ps^- Feshbach resonance becomes

$$F' = F_F\frac{\tau_{L\alpha}}{\tau_{Ps^-}} \approx 10\mu\text{J/cm}^2 \tag{15}$$

If the laser fluence is increased to 400 μJ/cm² the spectrum will be power broadened in proportion to the square root of the fluence [26] to ~40 GHz compared to the 400 GHz full width at half maximum Doppler broadening expected for a room temperature source of Ps^- [4]. One would then expect to observe a Feshbach resonance signal corresponding to about 10% of the total number of Ps^- ions present in the ground state. Given the large numbers of Ps^- ions produced using the alkali metal on tungsten method [4], this signal should be sufficient for a measurement of the center frequency of the lowest Ps^- Feshbach resonance with a precision of a few parts per million.

Conclusion

Modeling the Ps^- as a weakly bound electron in the presence of a slightly distorted positronium atom indicates that the dipole matrix element connecting the ground state with the lowest energy Feshbach resonance is nearly the same as in the case of exciting the Lyman-α transition in Ps. Based on this we have concluded that optical excitation of Ps^- to its lowest Feshbach resonance is feasible under typical experimental conditions.

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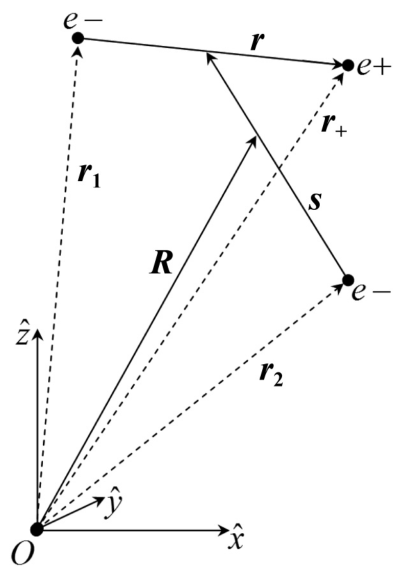
Appendix A

Here we present arguments in support of (3) and (4). We choose coordinates in Fig. A1 to emphasize that the Ps^- ion is in a singlet state relative to the two electrons, so that the Pauli principle is automatically satisfied for any two electron wave functions. In addition, there is no applied magnetic field and we neglect spin–orbit effects. In that case the Ps^- wave function may be accurately approximated by a bound state of three distinguishable spinless leptons. Because the Ps^- ion is weakly bound relative to a ground state Ps atom and a free electron of zero kinetic energy, we further simplify our problem by letting the ion be approximated by a distinguishable electron that is loosely bound to a Ps atom.

Fig. A1. Coordinates for the positronium negative ion. *O* is the origin of the coordinate system, $\boldsymbol{R}$ is the coordinate of the center of mass of the Ps^- ion, $\boldsymbol{r}$ is a vector drawn from the Ps electron to the positron, and $\boldsymbol{s}$ is a vector drawn from the ion electron to the Ps center of mass location. The coordinates of the positron and the two electrons are $\boldsymbol{r}_+$, $\boldsymbol{r}_1$, and $\boldsymbol{r}_2$, respectively.



The interaction with an applied electric field $\boldsymbol{E} = E_0\hat{z}\cos(\omega t)$ is

$$V = eE_0(\boldsymbol{r}_+ - \boldsymbol{r}_1 - \boldsymbol{r}_2)\cdot\hat{z} \tag{A1}$$

Because the wave functions of the Ps and the ion electron will be assumed not to depend on the position of the center of mass, the effective interaction potential may be written

$$V_{\text{eff}} = eE_0\left(\frac{2}{3}\boldsymbol{s} - \boldsymbol{r}\right)\cdot\hat{z} \tag{A2}$$

The Ps^- states, $|\Psi_{\mathscr{L}\mathscr{M}}(\boldsymbol{r},\boldsymbol{s})\rangle$, of total angular momentum $\mathscr{L}$ and azimuthal quantum number $\mathscr{M}$ may be written as sums of products of Ps and ion electron wave functions of various combinations of orbital angular momenta, such that each term has total angular momentum $\mathscr{L}$ and azimuthal quantum number $\mathscr{M}$. We denote the Ps states by

$$|\psi_{LM}(r)\rangle|L,M\rangle_{\text{Ps}} \tag{A3}$$

and the ion electron states by

$$|\phi_{LM}(s)\rangle|L,M\rangle_{\text{e}^-} \tag{A4}$$

where $\Psi_{LM}(r)$ and $\phi_{LM}(s)$ are the radial Ps and e^- wave functions of angular momentum L and azimuthal quantum number M determined by minimization of the energy based on the unperturbed Hamiltonian being the sum of the Coulomb potentials and the particle kinetic energies.

The Ps^- ground state with $\mathscr{L} = 0$ and $\mathscr{M} = 0$ will then be an infinite sum of terms

$$\begin{aligned}|\Psi_{00}(\boldsymbol{r},\boldsymbol{s})\rangle &= a|\psi_{00}(r)\rangle|0,0\rangle_{\text{Ps}}|\phi_{00}(s)\rangle|0,0\rangle_{\text{e}^-}\\ &\quad + b\sqrt{\frac{1}{3}}[|\psi_{11}(r)\rangle|1,1\rangle_{\text{Ps}}|\phi_{1-1}(s)\rangle|1,-1\rangle_{\text{e}^-}\\ &\quad + |\psi_{1-1}(r)\rangle|1,-1\rangle_{\text{Ps}}|\phi_{11}(s)\rangle|1,1\rangle_{\text{e}^-}\\ &\qquad - |\psi_{10}(r)\rangle|1,0\rangle_{\text{Ps}}|\phi_{10}(s)\rangle|1,0\rangle_{\text{e}^-}] + c\ldots\end{aligned} \tag{A5}$$

The oscillating electric field in the $\hat{z}$-direction can only couple the ground state to Feshbach resonance states with $\mathscr{L} = 1$ and $\mathscr{M} = 0$ represented by a wave function of the form

$$\begin{aligned}|\Psi_{10}(\boldsymbol{r},\boldsymbol{s})\rangle &= d|\psi'_{10}(r)\rangle|1,0\rangle_{\text{Ps}}|\phi'_{00}(s)\rangle|0,0\rangle_{\text{e}^-}\\ &\quad + e|\psi'_{00}(r)\rangle|0,0\rangle_{\text{Ps}}|\phi'_{10}(s)\rangle|1,0\rangle_{\text{e}^-}\\ &\quad + f\sqrt{\frac{1}{2}}[|\psi'_{11}(r)\rangle|1,1\rangle_{\text{Ps}}|\phi'_{1-1}(s)\rangle|1,-1\rangle_{\text{e}^-}\\ &\qquad - |\psi'_{1-1}(r)\rangle|1,-1\rangle_{\text{Ps}}|\phi'_{11}(s)\rangle|1,1\rangle_{\text{e}^-}] + g\ldots\end{aligned} \tag{A6}$$

where the primed wave functions are those for the Feshbach resonance state.

The dipole moment coupling the ground state with a state having $\mathscr{L} = 1$ and $\mathscr{M} = 0$ will be the matrix element

$$\begin{aligned}p_F &= \langle\Psi_{00}(\boldsymbol{r},\boldsymbol{s})|\left(\frac{2}{3}\boldsymbol{s} - \boldsymbol{r}\right)\cdot\hat{z}|\Psi_{10}(\boldsymbol{r},\boldsymbol{s})\rangle\\ &= a\langle\psi_{00}(r)|\langle 0,0|_{\text{Ps}}\langle\phi_{00}(s)|\langle 0,0|_{\text{e}^-}\left(\frac{2}{3}\boldsymbol{s} - \boldsymbol{r}\right)\cdot\hat{z}[d|\psi'_{10}(r)\rangle|1,0\rangle_{\text{Ps}}|\phi'_{00}(s)\rangle|0,0\rangle_{e^-} + e|\psi'_{00}(r)\rangle|0,0\rangle_{\text{Ps}}|\phi'_{10}(s)\rangle|1,0\rangle_{\text{e}^-}] + \cdots\\ &= a\langle\psi_{00}(r)|\langle 0,0|_{\text{Ps}}\langle\phi_{00}(s)|\langle 0,0|_{\text{e}^-}\left(\frac{2}{3}\boldsymbol{s} - \boldsymbol{r}\right)\cdot\hat{z}d|\psi'_{10}(r)\rangle|1,0\rangle_{\text{Ps}}|\phi'_{00}(s)\rangle|0,0\rangle_{\text{e}^-}\\ &\qquad + a\langle\psi_{00}(r)|\langle 0,0|_{\text{Ps}}\langle\phi_{00}(s)|\langle 0,0|_{\text{e}^-}\left(\frac{2}{3}\boldsymbol{s} - \boldsymbol{r}\right)\cdot e|\psi'_{00}(r)\rangle|0,0\rangle_{\text{Ps}}|\phi'_{10}(s)\rangle|1,0\rangle_{\text{e}^-} + \cdots\\ &= a\langle\psi_{00}(r)|\langle 0,0|_{\text{Ps}}\langle\phi_{00}(s)|\langle 0,0|_{\text{e}^-}(-\boldsymbol{r}\cdot\hat{z})d|\psi'_{10}(r)\rangle|1,0\rangle_{\text{Ps}}|\phi'_{00}(s)\rangle|0,0\rangle_{\text{e}^-}\\ &\qquad + a\langle\psi_{00}(r)|\langle 0,0|_{\text{Ps}}\langle\phi_{00}(s)|\langle 0,0|_{\text{e}^-}\left(\frac{2}{3}\boldsymbol{s}\cdot\hat{z}\right)e|\psi'_{00}(r)\rangle|0,0\rangle_{\text{Ps}}|\phi'_{10}(s)\rangle|1,0\rangle_{\text{e}^-} + \cdots\\ &= -ad\langle\psi_{00}(r)|r|\psi'_{10}(r)\rangle_{\text{Ps}}\langle\phi_{00}(s)|\phi'_{00}(s)\rangle + \frac{2}{3}ae\langle\psi_{00}(r)|\psi'_{00}(r)\rangle\langle\phi_{00}(s)|s|\phi'_{10}(s)\rangle + \cdots\end{aligned} \tag{A7}$$

In the approximation that the Feshbach resonance is mostly a 2P positronium atom surrounded by an S state ion electron, the coefficients a and d will be nearly unity and the other coefficients in the expansions of $|\Psi_{00}(\boldsymbol{r},\boldsymbol{s})\rangle$ and $|\Psi_{10}(\boldsymbol{r},\boldsymbol{s})\rangle$ may be neglected. We then have for the first-order approximation for the dipole moment

$$p_F = -\langle\psi_{00}(r)|r|\psi'_{10}(r)\rangle_{\mathrm{Ps}}\langle\phi_{00}(s)|\phi'_{00}(s)\rangle \tag{A8}$$

In the further approximation that the Ps wave functions in the presence of the weakly bound ion electron are roughly the same as in an isolated Ps atom, we then get

$$p_F = -p_{L\alpha}\langle\phi_{00}(s)|\phi'_{00}(s)\rangle \tag{A9}$$

which is identical, except for the sign, to (3).

The interaction potential in the Ps⁻ ion Hamiltonian in the absence of the laser electric field is

$$\begin{aligned}U(\boldsymbol{r},\boldsymbol{s}) &= \frac{e^2}{4\pi\varepsilon_0}\left(\left|\boldsymbol{s}-\frac{1}{2}\boldsymbol{r}\right|^{-1} - \left|\boldsymbol{s}+\frac{1}{2}\boldsymbol{r}\right|^{-1}\right)\\ &= \frac{e^2}{4\pi\varepsilon_0}\left(\frac{\boldsymbol{r}\cdot\hat{s}}{s^2}\right)\left[1-\frac{3}{8}\left(\frac{r}{s}\right)^2+\cdots\right]\end{aligned} \tag{A10}$$

This means that there is no first-order interaction between an $L = 0$ electron and a 2P Ps atom or an $L = 1$ electron and a 2S Ps atom. Therefore, the interaction potential will contribute to the Feshbach resonance binding energy only in second order. In this case the effective interaction for the ion electron with the 2P Ps atom will fall off as s^{-4}, thus justifying the approximate wave function in (4). In addition, the $L > 0$ electron wave functions are not going to be important to the Feshbach resonance state because the squares of these functions are proportional to s^{2L}, which inhibits their sampling the potential for small s where it is strongest. This means that the major component of the ion electron wave function in the Feshbach resonance state has $L = 0$, providing further justification for the approximations used to write (4).