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Fock-Tani representation for positron-hydrogen scattering

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A new second-quantization representation for low-energy positron-hydrogen scattering is derived by starting with the standard Fock representation and carrying out two canonical transformations, one to introduce the field operator for bound positronium and the other to introduce one for the bound atomic electron. The transformed "Fock-Tani representation" Hamiltonian is obtained in closed form. Its various terms have simple physical interpretations and manifest the various scattering and reaction channels. The interaction-matrix elements obtained are automatically renormalized through inclusion of bound-state–continuum orthogonality corrections. The definition of the S-matrix elements is simpler in the new representation since bound states are exactly redescribed therein as elementary particles. Certain constraints necessary and sufficient for the one-one property of the mapping from Fock- to Fock-Tani-state space are shown to be automatically satisfied when the asymptotic initial and final states for scattering processes are defined by the standard wave-packet method. This representation is expected to be useful for inclusion of the intermediate-state positronium channel in the standard many-body Green's-function approach to evaluation of S-matrix elements.

I. INTRODUCTION

Quantum-field-theoretic Green's functions have been shown to be a very useful tool for calculations of low-energy elastic and inelastic electron-atom, atom-atom, and atom-molecule scattering cross sections.[1–5] The S-matrices for such processes are expressible in terms of single-particle Green's functions.[2] Similar methods are also applicable to reactive scattering cross sections, but in such cases $(n',m'\leftarrow n,m)$ Bethe-Salpeter transition amplitudes[6] are required for the reactive S-matrix elements of a process involving n- and m-particle initial bound states and n'- and m'-particle final bound states. These are much harder to determine accurately than are single-particle Green's functions.

This difficulty can be circumvented by a change of representation (unitary transformation) such that in the new representation, the field operators for the composite bound states satisfy elementary-particle commutation relations and are therefore already manifested in appropriate $(1,1\leftarrow 1,1)$ particle transition amplitudes. In recent years several such representations have been developed. The one which will be discussed herein is the Fock-Tani representation, obtained from the standard Fock representation of the constituents (electrons and nuclei) by a suitable unitary transformation, the generalized Tani transformation.[7,8] The price paid for these advantages is the difficulty of carrying out the transformation in detail so as to obtain an explicit expression for the Fock-Tani Hamiltonian. In fact, in the cases previously discussed involving many-body systems of composite particles, the interaction Hamiltonian in the new representation is an infinite series of which only the leading terms are known explicitly. However, for some few-body systems, the transformation can be carried out exactly and explicitly. This is the case, for example, for positron-hydrogen scattering in the fixed-nucleus approximation. Then the bound composite species are the hydrogen atom (described as one electron bound to a force center, the proton) and the positronium atom. The representation thus obtained is expected to be particularly convenient for treating the effects of the positronium channel, which contributes importantly in virtual intermediate states in calculation of low-energy positron-hydrogen scattering cross sections, even before the real positronium channel opens.

A field-theoretic description of such effects using composite positronium fields and their Green's functions has been initiated by Ficocelli Varra-

chio.[9,6] However, calculations will be facilitated by a change of representation such that the positronium contributions are already included in lower-order Green's functions. This is the motivation for the derivation herein of the Fock-Tani Hamiltonian for positron-hydrogen scattering. Calculations using this representation will be described in subsequent publications.

In Sec. II the standard Fock representation for this system is introduced, and the Fock representation of the hydrogen and positronium bound states is described in Secs. III and IV. The transformation to the new Fock-Tani representation is carried out in Sec. V and Appendixes A–D, and the physical interpretation of the new representation is discussed. Certain constraints necessary and sufficient for the one-one property of the mapping from Fock to Fock-Tani state space are shown in Secs. VI and VII and Appendix E to be automatically satisfied when the asymptotic initial and final states for scattering processes are defined by the standard wave-packet method, and a simple definition of S-matrix elements in Fock-Tani representation is shown to be equivalent to the more complicated definition in terms of bound states in Fock space.

II. FOCK REPRESENTATION

The system of interest consists of one positron and one electron in the Coulomb field of a proton assumed fixed at the origin. Let $\hat{p}(x)$ and $\hat{e}(y)$ be the standard Fock representations of the positron and electron field operators. Here $x=(\vec{r}_p,\sigma_p)$ with $\vec{r}_p$ the positron position vector and $\sigma_p(=\uparrow$ or $\downarrow)$ its spin z-component variable. $\int dx$ stands for $\sum_{\sigma p}\int d^3\vec{r}_p$.

Similarly, $y=(\vec{r}_e,\sigma_e)$ and

$$\int dy=\sum_{\sigma e}\int d\vec{r}_e$$

for the electron. The standard nonrelativistic Fock Hamiltonian is

$$\hat{H}_F=\int dx\,\hat{p}^\dagger(x)H_p(x)\hat{p}(x)+\int dy\,\hat{e}^\dagger(y)H_e(y)\hat{e}(y)+\int dx\,dy\,\hat{p}^\dagger(x)\hat{e}^\dagger(y)V_{pe}(xy)\,\hat{e}(y)\hat{p}(x) \tag{1}$$

on the one-positron one-electron subspace. The advantages of such a Fock representation even for few-body scattering problems have already been amply demonstrated in the literature.[1–5] The Schrödinger operators occurring in (1) are given, in atomic units $\hbar=m=e=1$, by

$$H_e(y)=-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_e^{\,2}}-\frac{1}{r_e}\,,$$
$$H_p(x)=-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_p^{\,2}}+\frac{1}{r_p}\,, \tag{2}$$
$$V_{pe}(xy)=-\frac{1}{|\vec{r}_p-\vec{r}_e|}\,.$$

The electron and positron fields satisfy the standard anticommutation relations[10]

$$[\hat{e}(y),\hat{e}(y')]_+=[\hat{p}(x),\hat{p}(x')]_+=0\,,$$
$$[\hat{e}(y),\hat{e}^\dagger(y')]_+=\delta(y-y')=\delta(\vec{r}_e-\vec{r}_e')\delta_{\sigma_e\sigma_e'}\,, \tag{3}$$
$$[\hat{p}(x),\hat{p}^\dagger(x')]_+=\delta(x-x')=\delta(\vec{r}_p-\vec{r}_p')\delta_{\sigma_p\sigma_p'}\,,$$
$$[\hat{e}(y),\hat{p}(x)]_+=[\hat{e}(y),\hat{p}^\dagger(x)]_+=0\,.$$

The Hamiltonian (1) is general enough to describe low-energy elastic, inelastic, and reactive positron-hydrogen scattering. Radiative and e-p annihilation and pair creation channels could be easily added, but in the interests of simplicity they will be omitted here.

III. HYDROGEN BOUND STATES

The creation operator $\hat{A}_{ve}^\dagger$ for an electron in orbital $\varphi_{ve}(y)$ bound to the nucleus at the origin is

$$\hat{A}_{ve}^\dagger=\int dy\,\varphi_{ve}(y)\hat{e}^\dagger(y)\,, \tag{4}$$

and the Fock representation of the corresponding one-electron state is

$$|ve\rangle=\hat{A}_{ve}^\dagger|0\rangle\,, \tag{5}$$

where $|0\rangle$ is the Fock vacuum. The φ_{ve} could be either free or perturbed orbitals; it is not necessary to specify the choice here. It is only assumed that the set $\{\varphi_{ve}\}$ is orthonormal, but not necessarily complete.[11] The $\hat{A}_{ve}^\dagger$ and $\hat{A}_{ve}=(\hat{A}_{ve}^\dagger)^\dagger$ satisfy the anticommutation relations

$$[\hat{A}_{ve},\hat{A}_{v'e}]_+=[\hat{e}(y),\hat{A}_{ve}]_+=0\,,$$
$$[\hat{A}_{ve},\hat{A}_{v'e}^\dagger]_+=\delta_{vv'}\,, \tag{6}$$
$$[\hat{e}(y),\hat{A}_{ve}^\dagger]_+=\varphi_{ve}(y)\,,$$
$$[\hat{p}(x),\hat{A}_{ve}]_+=[\hat{p}(x),\hat{A}_{ve}^\dagger]_+=0\,.$$

IV. POSITRONIUM BOUND STATES

These are

$$|\alpha\,\mathrm{Ps}\rangle = \hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}|0\rangle\ , \tag{7}$$

where

$$\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}} = \int dx\,dy\,\varphi_{\alpha\,\mathrm{Ps}}(xy)\hat{p}^{\dagger}(x)\hat{e}^{\dagger}(y) \tag{8}$$

and the $\varphi_{\alpha\,\mathrm{Ps}}$ are the bound positronium wave functions; again, $x=(\vec{r}_p,\sigma_p)$ and $y=(\vec{r}_e,\sigma_e)$. The $\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}$ and $\hat{A}_{\alpha\,\mathrm{Ps}}=(\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}})^{\dagger}$ satisfy the commutation relations

$$\begin{aligned}
&[\hat{A}_{\alpha\,\mathrm{Ps}},\hat{A}_{\beta\,\mathrm{Ps}}]_- = [\hat{p}(x),\hat{A}_{\alpha\,\mathrm{Ps}}]_- = [\hat{e}(y),\hat{A}_{\alpha\,\mathrm{Ps}}]_- = 0\ ,\\
&[\hat{A}_{\alpha\,\mathrm{Ps}},\hat{A}^{\dagger}_{\beta\,\mathrm{Ps}}]_- = \delta_{\alpha\beta} + \hat{C}_{\alpha\beta}\ ,\\
&[\hat{p}(x),\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}]_- = \int dy\,\varphi_{\alpha\,\mathrm{Ps}}(xy)\hat{e}^{\dagger}(y)\ ,\\
&[\hat{e}(y),\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}]_- = -\int dx\,\varphi_{\alpha\,\mathrm{Ps}}(xy)\hat{p}^{\dagger}(x)\ ,
\end{aligned} \tag{9}$$

assuming the $\varphi_{\alpha\,\mathrm{Ps}}$ orthonormal. The operator $\hat{C}_{\alpha\beta}$ is

$$\begin{aligned}
\hat{C}_{\alpha\beta} = &-\int dy_1 dy_2 K^{(e)}_{\alpha\beta}(y_1,y_2)\hat{e}^{\dagger}(y_1)\hat{e}(y_2)\\
&-\int dx_1 dx_2 K^{(p)}_{\alpha\beta}(x_1,x_2)\hat{p}^{\dagger}(x_1)\hat{p}(x_2)\ ,
\end{aligned} \tag{10}$$

where the electron and positron exchange kernels are

$$\begin{aligned}
K^{(e)}_{\alpha\beta}(y_1,y_2) &= \int \varphi^{*}_{\alpha\,\mathrm{Ps}}(xy_2)\varphi_{\beta\,\mathrm{Ps}}(xy_1)dx\ ,\\
K^{(p)}_{\alpha\beta}(x_1,x_2) &= \int \varphi^{*}_{\alpha\,\mathrm{Ps}}(x_2y)\varphi_{\beta\,\mathrm{Ps}}(x_1y)dy\ .
\end{aligned} \tag{11}$$

V. FOCK-TANI REPRESENTATION

We shall transform to a new representation in which the bound atomic electron and positronium states are described by annihilation and creation operators $\hat{e}_\nu$, $\hat{e}^{\dagger}_\nu$ (electrons) and $\hat{\psi}_\alpha$, $\hat{\psi}^{\dagger}_\alpha$ (positronium) which are kinematically independent of the free electron and positron operators $\hat{e}(y)$, $\hat{e}^{\dagger}(y)$, $\hat{p}(x)$, and $\hat{p}^{\dagger}(x)$ in the sense that the anticommutation and commutation relations (6) and (9) involving the $\hat{A}_{\nu e}$, $\hat{A}^{\dagger}_{\nu e}$, $\hat{A}_{\alpha\,\mathrm{Ps}}$, and $\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}$ are replaced by

$$\begin{aligned}
&[\hat{e}_\nu,\hat{e}_{\nu'}]_+ = [\hat{e}(y),\hat{e}_\nu]_+ = 0\ ,\\
&[\hat{\psi}_\alpha,\hat{\psi}_\beta]_- = [\hat{p}(x),\hat{\psi}_\alpha]_- = [\hat{e}(y),\hat{\psi}_\alpha]_- = 0\ ,\\
&[\hat{e}_\nu,\hat{\psi}_\alpha]_- = [\hat{e}_\nu,\hat{\psi}^{\dagger}_\alpha]_- = 0\ ,\\
&[\hat{e}_\nu,\hat{e}^{\dagger}_{\nu'}]_+ = \delta_{\nu\nu'},\quad [\hat{\psi}_\alpha,\hat{\psi}^{\dagger}_\beta]_- = \delta_{\alpha\beta}\ ,\\
&[\hat{e}(y),\hat{e}^{\dagger}_\nu]_+ = [\hat{p}(x),\hat{\psi}^{\dagger}_\alpha]_- = 0\ ,\\
&[\hat{p}(x),\hat{e}_\nu]_+ = [\hat{p}(x),\hat{e}^{\dagger}_\nu]_+ = 0\ ,\\
&[\hat{e}(y),\hat{\psi}^{\dagger}_\nu]_- = 0\ .
\end{aligned} \tag{12}$$

The procedure for enlargement of the Fock space so as to allow consistent imposition of these commutation and anticommutation relations along with (3), (6), and (9) is discussed in Appendix A. Note that the set of positronium quantum numbers can be decomposed as $\alpha=(\vec{k},\nu)$ where $\vec{k}$ is the translational wave vector and ν the set of internal atomic quantum numbers, the same as the set ν of atomic quantum numbers labeling the atomic electron orbitals $\varphi_{\nu e}$. This corresponds to the usual center-of-mass decomposition of the positronium wave functions

$$\varphi_{\alpha\,\mathrm{Ps}}(xy) = (2\pi)^{-3/2} e^{\,i\vec{k}\cdot\vec{r}}\, u_\nu(\vec{r}_e-\vec{r}_p,\sigma_p,\sigma_e) \tag{13}$$

with $\vec{r}=\frac{1}{2}(\vec{r}_e+\vec{r}_p)$. The $\delta_{\alpha\beta}$ in (9) stands for $\delta(\vec{k}-\vec{k}')\delta_{\nu\nu'}$ where $\alpha=(\vec{k},\nu)$ and $(\beta=(\vec{k}',\nu')$. By Fourier transformation with respect to $\vec{k}$, one can introduce field operators $\hat{\psi}_\nu(\vec{r})$, $\hat{\psi}^{\dagger}_\nu(\vec{r})$ for positronium in internal state ν with center of mass localized at $\vec{r}$:

$$\begin{aligned}
\hat{\psi}_\nu(\vec{r}) &= (2\pi)^{-3/2}\int d\vec{k}\, e^{\,i\vec{k}\cdot\vec{r}}\hat{\psi}_{k\nu}\ ,\\
\hat{\psi}_{\vec{k}\,\nu} &= (2\pi)^{-3/2}\int d\vec{r}\, e^{-i\vec{k}\cdot\vec{r}}\hat{\psi}_\nu(\vec{r})\ .
\end{aligned} \tag{14}$$

Here $\hat{\psi}_{\vec{k}\,\nu}=\hat{\psi}_\alpha$ with $\alpha=(\vec{k},\nu)$. The positronium field operators satisfy the local Bose commutation relation

$$[\hat{\psi}_\nu(\vec{r}),\hat{\psi}^{\dagger}_{\nu'}(\vec{r}')]_- = \delta(\vec{r}-\vec{r}')\delta_{\nu\nu'} \tag{15}$$

in spite of the finite size and composite structure of the positronium atom. Note that this would not be the case for the Fourier transforms of the composite positronium operators $\hat{A}_{\alpha\,\mathrm{Ps}}$, due to the $\hat{C}_{\alpha\beta}$ operator term in the commutation relation (9). This is a major motivation for carrying out a change of representation to the "Fock-Tani state space" in which the simpler relations (12) are valid.

The desired change of representation is effected by the multispecies generalization of the Tani transformation[12] which has already been discussed in detail.[7] The unitary operator $\hat{U}$ which effects the change of representation is

$$\begin{aligned}
&\hat{U} = \hat{U}_{\mathrm{Ps}}\hat{U}_e\ ,\\
&\hat{U}_{\mathrm{Ps}} = \exp\left[\frac{\pi}{2}\hat{F}_{\mathrm{Ps}}\right],\ \hat{F}_{\mathrm{Ps}} = \sum_\alpha (\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}\hat{\psi}_\alpha - \hat{\psi}^{\dagger}_\alpha\hat{A}_{\alpha\,\mathrm{Ps}})\ ,\\
&\hat{U}_e = \exp\left[\frac{\pi}{2}\hat{F}_e\right],\ \hat{F}_e = \sum_\nu (\hat{A}^{\dagger}_{\nu e}\hat{e}_\nu - \hat{e}^{\dagger}_\nu\hat{A}_{\nu e})\ .
\end{aligned} \tag{16}$$

Then[7]

$$\hat{U}^{-1}|\nu e\rangle=\hat{U}^{-1}\hat{A}^{\dagger}_{\nu e}|0\rangle=|\nu e\rangle\equiv\hat{e}^{\dagger}_{\nu}|0\rangle\ ,$$
$$\hat{U}^{-1}|\alpha\,\mathrm{Ps}\rangle=\hat{U}^{-1}\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}|0\rangle=|\alpha\,\mathrm{Ps}\rangle\equiv\hat{\psi}^{\dagger}_{\alpha}|0\rangle\ , \tag{17}$$

i.e., a bound atomic electron and bound positronium atom are redescribed as kinematically independent elementary particles in this new representation.[13] Note that $\hat{U}_{\mathrm{Ps}}$ and $\hat{U}_e$ do not commute. The ordering $\hat{U}_{\mathrm{Ps}}\hat{U}_e$ is essential; for the opposite order $\hat{U}_e\hat{U}_{\mathrm{Ps}}$, the second Eq. (17) is violated; see Ref. 7. $\hat{U}$ acts on an enlarged state space $\mathscr{S}$ which is a "graded direct product" of the original electron-positron Fock space $\mathscr{F}$ and a new Fock space $\mathscr{B}$ of the operators $\hat{e}_{\nu}$, $\hat{e}^{\dagger}_{\nu}$, $\hat{\psi}_{\alpha}$, and $\hat{\psi}^{\dagger}_{\alpha}$, as discussed in Appendix A. A subspace $\mathscr{S}_0$ of $\mathscr{S}$, defined by the constraints

$$\hat{N}_a|\ \rangle=\hat{N}_{\mathrm{Ps}}|\ \rangle=0,\quad|\ \rangle\in\mathscr{S}_0 \tag{18}$$

is isomorphic with $\mathscr{F}$. Here $\hat{N}_a$ and $\hat{N}_{\mathrm{Ps}}$ are the number operators for bound atomic electrons and positronium atoms in the new representation

$$\hat{N}_a=\sum_{\nu}\hat{e}^{\dagger}_{\nu}\hat{e}_{\nu},\quad\hat{N}_{\mathrm{Ps}}=\sum_{\alpha}\hat{\psi}^{\dagger}_{\alpha}\hat{\psi}_{\alpha}\ . \tag{19}$$

As will be discussed in Sec. VI, after the change of representation affected by $\hat{U}$, the trivial constraints (18) will be replaced by new constraints expressing the fact that in the new Fock-Tani representation, bound atomic electrons and positronium atoms are described by the operators $\hat{e}_{\nu}$, $\hat{e}^{\dagger}_{\nu}$, $\hat{\psi}_{\alpha}$, and $\hat{\psi}^{\dagger}_{\alpha}$ rather than $\hat{A}_{\nu e}$, $\hat{A}^{\dagger}_{\nu e}$, $\hat{A}_{\alpha\,\mathrm{Ps}}$, and $\hat{A}^{\dagger}_{\alpha\,\mathrm{Ps}}$.

The Hamiltonian $\hat{H}$ in Fock-Tani representation is

$$\hat{H}=\hat{U}^{-1}\hat{H}_F\hat{U}=\hat{U}_e^{-1}(\hat{U}_{\mathrm{Ps}}^{-1}\hat{H}_F\hat{U}_{\mathrm{Ps}})\hat{U}_e \tag{20}$$

with $\hat{H}_F$ the one-positron one-electron[14] Fock Hamiltonian (1). The evaluation of the positronium Tani transformation $\hat{U}_{\mathrm{Ps}}^{-1}\hat{H}_F\hat{U}_{\mathrm{Ps}}$ is carried out in Appendix B; the result is

$$\begin{aligned}\hat{U}_{\mathrm{Ps}}^{-1}\hat{H}_F\hat{U}_{\mathrm{Ps}}=&\sum_{\alpha\beta}\hat{\psi}^{\dagger}_{\alpha}(\alpha|H_{pe}|\beta)\hat{\psi}_{\beta}+\sum_{\alpha}\int dx\,dy[\hat{p}^{\dagger}(x)\hat{e}^{\dagger}(y)(xy|H_{pe}|\alpha)'\hat{\psi}_{\alpha}+\mathrm{H.c.}]\\&+\int dx\,\hat{p}^{\dagger}(x)H_p(x)\hat{p}(x)+\int dy\,\hat{e}^{\dagger}(y)H_e(y)\hat{e}(y)\\&+\int dx\,dy\,dx'dy'\hat{p}^{\dagger}(x)\hat{e}^{\dagger}(y)(xy|H_{pe}|x'y')'\hat{e}(y')\hat{p}(x')\ .\end{aligned} \tag{21}$$

Here $(\alpha|H_{pe}|\beta)$ is the matrix element of H_{pe} between bound positronium wave functions

$$(\alpha|H_{pe}|\beta)=\int\varphi^{*}_{\alpha\,\mathrm{Ps}}(xy)H_{pe}(xy)\varphi_{\beta\,\mathrm{Ps}}(xy)dx\,dy \tag{22}$$

with H_{pe} the Hamiltonian of the positron and electron *in the field of the proton*

$$H_{pe}(xy)=H_p(x)+H_e(y)+V_{pe}(xy) \tag{23}$$

[see (2)]. $(\alpha|H_{pe}|xy)'$ and $(xy|H_{pe}|\alpha)'$ are renormalized matrix elements for positronium formation and decay,

$$\begin{aligned}(xy|H_{pe}|\alpha)'&=H_{pe}(xy)\varphi_{\alpha\,\mathrm{Ps}}(xy)-\int\Delta_{\mathrm{Ps}}(xy,x'y')H_{pe}(x'y')\varphi_{\alpha\,\mathrm{Ps}}(x'y')dx'dy'\ ,\\(\alpha|H_{pe}|xy)'&=[(xy|H_{pe}|\alpha)']^{*}\ ,\end{aligned} \tag{24}$$

and $(xy|H_{pe}|x'y')'$ is a renormalized, nonlocal positron-electron interaction-matrix element

$$\begin{aligned}(xy|H_{pe}|x'y')'=&V_{pe}(xy)\delta(x-x')\delta(y-y')-[H_{pe}(xy)+H_{pe}(x'y')]\Delta_{\mathrm{Ps}}(xy,x'y')\\&+\int\Delta_{\mathrm{Ps}}(xy,x''y'')H_{pe}(x''y'')\Delta_{\mathrm{Ps}}(x''y'',x'y')dx''dy''\ .\end{aligned} \tag{25a}$$

The function Δ_{Ps} in these expressions is the positronium bound-state kernel explicitly given by

$$\Delta_{\mathrm{Ps}}(x_1y_1,x_2y_2)=\sum_{\alpha}\varphi_{\alpha\,\mathrm{Ps}}(x_1y_1)\varphi^{*}_{\alpha\,\mathrm{Ps}}(x_2y_2)\ . \tag{25b}$$

These expressions simplify if the $\varphi_{\alpha\,\mathrm{Ps}}(xy)$ are taken to be the bound positronium energy eigenstates in the absence of the field of the proton, satisfying the Schrödinger equation

$$\left[-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_p^{\,2}}-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_e^{\,2}}-\frac{1}{|\vec{r}_p-\vec{r}_e|}\right]\varphi_{\alpha\,\mathrm{Ps}}(xy)=\epsilon_{\alpha}\varphi_{\alpha\,\mathrm{Ps}}(xy)\ . \tag{26}$$

Then it is easy to show, using the definition (B23) of $\Delta_{\rm Ps}$ and the identities (B24), that

$$
\begin{aligned}
&(\alpha \mid H_{pe} \mid \beta)=\epsilon_\alpha \delta_{\alpha\beta}+(\alpha \mid V_{\rm prot} \mid \beta) ,\\
&(xy \mid H_{pe} \mid \alpha)' =(xy \mid V_{\rm prot} \mid \alpha)' ,\\
&(xy \mid H_{pe} \mid x'y')' = V_{pe}(xy)\delta(x-x')\delta(y-y')\\
&\qquad -\sum_\alpha \epsilon_\alpha \varphi_{\alpha\,{\rm Ps}}(xy)\varphi^*_{\alpha\,{\rm Ps}}(x'y')\\
&\qquad +(xy \mid V_{\rm prot} \mid x'y')' ,
\end{aligned}
\tag{27}
$$

where $(\alpha \mid V_{\rm prot} \mid \beta)$ is the matrix element for positronium transitions[15] due to the Coulomb field of the proton

$$
(\alpha \mid V_{\rm prot} \mid \beta)=\int \varphi^*_{\alpha\,{\rm Ps}}(xy)\left[\frac{1}{r_p}-\frac{1}{r_e}\right]\times\varphi_{\beta\,{\rm Ps}}(xy)dx\,dy \tag{28}
$$

$(xy \mid V_{\rm prot} \mid \alpha)'$ and its complex conjugate $(\alpha \mid V_{\rm prot} \mid xy)'$ are renormalized matrix elements for positronium decay and formation due to the field of the proton,

$$
(xy \mid V_{\rm prot} \mid \alpha)' = \left[\frac{1}{r_p}-\frac{1}{r_e}\right]\varphi_{\alpha\,{\rm Ps}}(xy)-\int \Delta_{\rm Ps}(xy,x'y')\left[\frac{1}{r'_p}-\frac{1}{r'_e}\right]\varphi_{\alpha\,{\rm Ps}}(x'y')dx'dy' , \tag{29}
$$

and $(xy \mid V_{\rm prot} \mid x'y')'$ is a renormalized matrix element for continuum-continuum positron-electron transitions due to the field of the proton

$$
\begin{aligned}
(xy \mid V_{\rm prot} \mid x'y')' =& -\left[\frac{1}{r_p}-\frac{1}{r_e}+\frac{1}{r'_p}-\frac{1}{r'_e}\right]\Delta_{\rm Ps}(xy,x'y')\\
&+\int \Delta_{\rm Ps}(xy,x''y'')\left[\frac{1}{r''_p}-\frac{1}{r''_e}\right]\Delta_{\rm Ps}(x''y'',x'y')dx''dy'' .
\end{aligned}
\tag{30}
$$

Note that the matrix elements $(xy \mid V_{\rm prot} \mid \alpha)'$ [Eq. (29)] and $(xy \mid H_{pe} \mid x'y')'$ [Eqs. (27) and (28)] both contain orthogonalization terms involving the positronium bound-state kernel $\Delta_{\rm Ps}$ [Eq. (B23)] in addition to their leading terms, the bare matrix elements. These orthogonalization terms are a direct consequence of the algebra of the transformation $\hat{U}_{\rm Ps}$, and express the fact that the continuum positron-electron wave functions are orthogonal to the bound positronium wave functions $\varphi_{\alpha\,{\rm Ps}}$. Since these orthogonalization terms are subtracted from the bare matrix elements, the renormalized matrix elements $(xy \mid V_{\rm prot} \mid \alpha)'$ and $(xy \mid H_{pe} \mid x'y')'$ are considerably smaller than the corresponding bare matrix elements, the strong internal positronium binding effects being already included in the diagonal term $\sum_\alpha \epsilon_{\alpha\,{\rm Ps}}\hat{\psi}^\dagger_\alpha\hat{\psi}_\alpha$.

To obtain the final expression for the Fock-Tani representation Hamiltonian $\hat{H}$ [Eq. (20)], one must apply the transformation $\hat{U}_e$ to (21) so as to introduce the annihilation and creation operators $\hat{e}_\nu$ and $\hat{e}^\dagger_\nu$ for the electron bound to the proton. There is a simple closed-form expression[12,16] for the effect of the transformation $\hat{U}_e$ on the electron field operator $\hat{e}(y)$:

$$
\hat{U}_e^{-1}\hat{e}(y)\hat{U}_e=\hat{e}(y)-\int dy'\Delta_e(y,y')\hat{e}(y')+\sum_\nu \varphi_{\nu e}(y)\hat{e}_\nu , \tag{31}
$$

where Δ_e is the hydrogen bound-state kernel

$$
\Delta_e(y,y')=\sum_\nu \varphi_{\nu e}(y)\varphi^*_{\nu e}(y') , \tag{32}
$$

a one-particle analog of the positronium bound-state kernel (B23). For completeness, the derivation of (31) is outlined in Appendix C. It follows from the anticommutation and commutation relations (6), (9), and (12) that $\hat{p}(x)$ and $\hat{\psi}_\alpha$ both commute with $\hat{F}_e$ [Eq. (16)]; hence they are invariant under the transformation

$$
\hat{U}_e^{-1}\hat{p}(x)\hat{U}_e=\hat{p}(x),\quad \hat{U}_e^{-1}\hat{\psi}_\alpha\hat{U}_e=\hat{\psi}_\alpha . \tag{33}
$$

It is then a straightforward matter to carry out the transformation (20) of (21) to obtain the Fock-Tani Hamiltonian

$$\hat{H}=\hat{U}_e^{-1}\hat{U}_{\rm Ps}^{-1}\hat{H}_F\hat{U}_{\rm Ps}\hat{U}_e=\hat{H}_0+\hat{V}\ ,$$

$$\hat{H}_0=\sum_\nu \epsilon_{\nu e}\hat{e}_\nu^\dagger\hat{e}_\nu+\int dy\,\hat{e}^\dagger(y)T_e(y)\hat{e}(y)+\sum_\alpha \epsilon'_\alpha\hat{\psi}_\alpha^\dagger\hat{\psi}_\alpha+\int dx\,\hat{p}^\dagger(x)T_p(x)\hat{p}(x)\ ,$$

$$\begin{aligned}V=&\int dy\,dy'\hat{e}^\dagger(y)(y\mid V_e\mid y')'\,\hat{e}(y')+\int dx\,\hat{p}^\dagger(x)\frac{1}{r_p}\hat{p}(x)+\sum_{\alpha\beta}{}'\,\hat{\psi}_\alpha^\dagger(\alpha\mid V_{\rm prot}\mid\beta)\hat{\psi}_\beta\\&+\sum_\alpha\int dx\,dy[\hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy\mid V_{\rm prot}\mid\alpha)''\,\hat{\psi}_\alpha+{\rm H.c.}]\\&+\sum_{\alpha\nu}\int dx[\hat{p}^\dagger(x)\hat{e}_\nu^\dagger(x\nu\mid V_{\rm prot}\mid\alpha)'\,\hat{\psi}_\alpha+{\rm H.c.}]\\&+\int dx\,dy\,dx'dy'\hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy\mid H_{pe}\mid x'y')''\,\hat{e}(y')\hat{p}(x')\\&+\sum_\nu\int dx\,dy\,dx'[\hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy\mid H_{pe}\mid x'\nu)''\,\hat{e}_\nu\hat{p}(x')+{\rm H.c.}]\\&+\sum_{\nu\nu'}\int dx\,dx'\hat{p}^\dagger(x)\hat{e}_\nu^\dagger(x\nu\mid H_{pe}\mid x'\nu')'\,\hat{e}_{\nu'}\hat{p}(x')\ .\end{aligned}\tag{34}$$

In deriving this expression it has been assumed that the $\varphi_{\alpha\,\rm Ps}$ satisfy (26) so that Eqs. (27)–(30) hold, and also that the $\varphi_{\nu e}$ are the unperturbed bound hydrogen orbitals satisfying the Schrödinger equation

$$H_e(y)\varphi_{\nu e}(y)=\left[-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_e{}^2}-\frac{1}{r_e}\right]\varphi_{\nu e}(y)=\epsilon_{\nu e}\varphi_{\nu e}(y)\ .\tag{35}$$

There are no $\hat{e}^\dagger(y)\hat{e}_\alpha$ and $\hat{e}_\alpha^\dagger\hat{e}(y)$ terms in the case that (35) is satisfied, because the renormalized matrix element

$$\begin{aligned}(y\mid H_e\mid\nu)'&=H_e(y)\varphi_{\nu e}(y)\\&\quad-\int\Delta_e(y,y')H_e(y')\varphi_{\nu e}(y')dy'\end{aligned}\tag{36}$$

then vanishes, in analogy with the simplification (27) of $(xy\mid H_{pe}\mid\alpha)'$ [Eq. (24)] ensuing when (26) is satisfied. To prove that (36) vanishes in the case (35), one employs the identity

$$\int\Delta_e(y,y')\varphi_{\nu e}(y')dy'=\varphi_{\nu e}(y)\tag{37}$$

analogous to (B24). The renormalized positronium energy levels ϵ'_α include the diagonal contribution from interaction with the proton

$$\epsilon'_\alpha=\epsilon_\alpha+(\alpha\mid V_{\rm prot}\mid\alpha)\ .\tag{38}$$

T_e and T_p are the electron and positron kinetic-energy operators

$$T_e(y)=-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_e^{\,2}},\quad T_p(x)=-\frac{1}{2}\frac{\partial^2}{\partial\vec{r}_p^{\,2}}\ .\tag{39}$$

The renormalized matrix element $(y\mid V_e\mid y')'$ for interaction of free (i.e., continuum) electrons with the proton is

$$\begin{aligned}(y\mid V_e\mid y')'=&-\frac{1}{r_e}\delta(y-y')\\&-\sum_\nu\epsilon_{\nu e}\varphi_{\nu e}(y)\varphi_{\nu e}^*(y')\ .\end{aligned}\tag{40}$$

The renormalization term subtracted $\sum_\nu\epsilon_{\nu e}\varphi_{\nu e}\varphi_{\nu e}^*$ is the part of the spectral representation of the one-electron Hamiltonian associated with its bound states, which are included in $\hat{H}_0$ in the term $\sum_\nu\epsilon_{\nu e}\hat{e}_\nu^\dagger\hat{e}_\nu$. The renormalized matrix element is therefore considerably smaller than the bare one, its first term; note the similar subtraction in the free positron-electron matrix element (27). The matrix element (27) undergoes a further renormalization in (34):

$$\begin{aligned}(xy\mid H_{pe}\mid x'y')''=&(xy\mid H_{pe}\mid x'y')'-\int\Delta_e(y,y_1)(xy_1\mid H_{pe}\mid x'y_1)'\,dy_1\\&-\int(xy\mid H_{pe}\mid x'y_1)'\,\Delta_e(y_1,y')dy_1+\int\Delta_e(y,y_1)(xy_1\mid H_{pe}\mid x'y_z)'\,\Delta_e(y_2,y')dy_1dy_2\ ,\end{aligned}\tag{41}$$

where the double prime indicates that this matrix element is renormalized by orthogonalization to both bound positronium and hydrogen (the latter orthogonalization involving Δ_e). The other matrix elements are

$$
\begin{aligned}
&(xy \mid V_{\text{prot}} \mid \alpha)'' = (xy \mid V_{\text{prot}} \mid \alpha)' - \int \Delta_e(y,y')(xy' \mid V_{\text{prot}} \mid \alpha)' dy' , \\
&(x\nu \mid V_{\text{prot}} \mid \alpha)' = \int \varphi^*_{\nu e}(y)(xy \mid V_{\text{prot}} \mid \alpha)' dy , \\
&(xy \mid H_{pe} \mid x'\nu')'' = \int [(xy \mid H_{pe} \mid x'y')' - \int \Delta_e(y,y'')(xy'' \mid H_{pe} \mid x'y')' dy'']\varphi_{\nu' e}(y')dy' , \\
&(x\nu \mid H_{pe} \mid x'\nu')' = \int \varphi^*_{\nu e}(y)(xy \mid H_{pe} \mid x'y')' \varphi_{\nu' e}(y')dy\, dy' .
\end{aligned}
\tag{42}
$$

Again, the single prime denotes renormalization by orthogonalization to positronium only, whereas the double prime denotes renormalization by orthogonalization to both positronium and hydrogen.

It can be shown[16] that the matrix-element orthogonalizations to hydrogen are equivalent to the description of the continuum electron by orthogonalized plane waves (plane waves with their projection onto the bound states subtracted) rather than undistorted plane waves. Such a description has been advocated previously in atomic physics, e.g., in the theory of photoionization.[17] Orthogonality constraints have been shown to play a fundamental role also in the theory of electron-atom scattering. In that case such constraints usually arise from distorted-wave formulations[18] based on optical potential descriptions of the interaction.[19] The present theory differs from such approaches and it seems closer in spirit to a formalism of "renormalized interactions" recently proposed in nuclear physics,[20] in order to exclude occupied states from optical amplitudes and potentials. The representation (34) can be regarded as a generalization of the orthogonalized plane-wave (OPW) formalism to include orthogonalizations of the free positron and electron wave functions to bound positronium. In the representation (34), such orthogonalization terms are included in the matrix elements rather than the field operators. One could use projected field operators instead. For example, the projected electron field operator $\hat{e}_\perp(y)$ is[21,22]

$$
\hat{e}_\perp(y) = \hat{e}(y) - \int dy' \Delta_e(y,y')\hat{e}(y') . \tag{43}
$$

However, inclusion of the orthogonalization terms in the matrix elements rather than the field operators has the advantage that the free-field operators have simpler algebraic properties than projected ones.

The positronium atom virtually present in intermediate states contributing to the positron-hydrogen scattering matrix elements is formed only in the neighborhood of the proton, since the electron is localized in that neighborhood in the initial state. There are, therefore, calculational advantages to expressing the positronium terms in (34) in terms of the position-space positronium field operator $\hat{\psi}_\nu(\vec{r})$. Such an expression is easily derived using (14); the result is

$$
\begin{aligned}
\hat{H}_0 &= \sum_\nu \epsilon_{\nu e}\hat{e}^\dagger_\nu\hat{e}_\nu + \int dy\, \hat{e}^\dagger(y)T_e(y)\hat{e}(y) + \int dx\, \hat{p}^\dagger(x)T_p(x)\hat{p}(x) + \sum_\nu \int d\vec{r}\, \hat{\psi}^\dagger_\nu(\vec{r}) \left[-\frac{1}{4}\frac{\partial^2}{\partial \vec{r}^2} + \epsilon'_{\nu\text{Ps}} \right] \hat{\psi}_\nu(\vec{r}) , \\
\hat{V} &= \int dy\, dy' \hat{e}^\dagger(y)(y \mid V_e \mid y')' \hat{e}(y') + \int dx\, \hat{p}^\dagger(x)\frac{1}{r_p}\hat{p}(x) + \sum_{\nu\nu'}{}' \int d\vec{r}\, \hat{\psi}^\dagger_\nu(\vec{r})(\vec{r}\nu \mid V_{\text{prot}} \mid \vec{r}\nu')\hat{\psi}_{\nu'}(\vec{r}) \\
&\quad + \sum_{\nu\sigma_p\sigma_e} \int d\vec{r}\, d\vec{r}_p\, d\vec{r}_e [\hat{p}^\dagger(\vec{r}_p\sigma_p)\hat{e}^\dagger(\vec{r}_e\sigma_e)(\vec{r}_p\sigma_p, r_e\sigma_e \mid V_{\text{prot}} \mid \vec{r}\nu)'' \hat{\psi}_\nu(\vec{r}) + \text{H.c.}] \\
&\quad + \sum_{\nu\nu'\sigma_p} \int d\vec{r}\, d\vec{r}_p [\hat{p}^\dagger(\vec{r}_p\sigma_p)\hat{e}^\dagger_\nu(r_p\sigma_p, \nu \mid V_{\text{prot}} \mid \vec{r}\nu')' \hat{\psi}_{\nu'}(\vec{r}) + \text{H.c.}] \\
&\quad + \int dx\, dy\, dx' dy' \hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy \mid H_{pe} \mid x'y')'' \hat{e}(y')\hat{p}(x') \\
&\quad + \sum_\nu \int dx\, dy\, dx' [\hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy \mid H_{pe} \mid x'\nu)'' \hat{e}_\nu \hat{p}(x') + \text{H.c.}] \\
&\quad + \sum_{\nu\nu'} \int dx\, dx' \hat{p}^\dagger(x)\hat{e}^\dagger_\nu(x\nu \mid H_{pe} \mid x'\nu')' \hat{e}_{\nu'}\hat{p}(x') .
\end{aligned}
\tag{44}
$$

One would, of course, be free to transfer the positron-proton interaction term $\hat{p}^\dagger(1/r_p)\hat{p}$ and part or all of the electron-proton interaction term $\hat{e}^\dagger(\ )'\hat{e}$ from $\hat{V}$ to $\hat{H}_0$ so that the eigenstates of $\hat{H}_0$ are Coulomb waves rather than plane waves. The same remark applies also to Eq. (34). In the term $\hat{\psi}_\nu^\dagger(\cdots)\hat{\psi}_\nu$ in $\hat{H}_0$, the operator $-(\frac{1}{4})\partial^2/\partial\vec{r}^2$ is the translational kinetic energy operator of the positronium atom, which has mass 2 in atomic units (electron mass = positron mass = 1). The $\epsilon'_{\nu\mathrm{Ps}}$ are renormalized positronium energy levels including the diagonal contribution from the positronium-proton interaction

$$\epsilon'_{\nu\mathrm{Ps}}=\epsilon_{\nu\mathrm{Ps}}+(\vec{r}\nu\mid V_{\mathrm{prot}}\mid\vec{r}\nu)\ . \tag{45}$$

The bare positronium levels $\epsilon_{\nu\mathrm{Ps}}$ are the internal contribution in the decomposition of the energy ϵ_α of the positronium wave function (13) into translational kinetic energy and internal contributions, where $\alpha=(\vec{k},\nu)$ with $\vec{k}$ the translational wave vector

$$\epsilon_\alpha=\epsilon_{\vec{k},\nu}=\tfrac{1}{4}\vec{k}^2+\epsilon_{\nu\mathrm{Ps}}\ . \tag{46}$$

The positronium-proton interaction-matrix element is

$$(\vec{r}\nu\mid V_{\mathrm{prot}}\mid\vec{r}\nu')=\sum_{\sigma_p\sigma_e}\int d^3\vec{r}_{ep}\,u_\nu^*(\vec{r}_{ep},\sigma_p,\sigma_e)\left[\frac{1}{|\vec{r}-\frac{1}{2}\vec{r}_{ep}|}-\frac{1}{|\vec{r}+\frac{1}{2}\vec{r}_{ep}|}\right]u_{\nu'}(\vec{r}_{ep},\sigma_p,\sigma_e)\ , \tag{47}$$

where u_ν is the internal wave function in the center-of-mass decomposition (13) and $\vec{r}_{ep}$ is the relative coordinate $\vec{r}_e-\vec{r}_p$. Recall that $\vec{r}$ is the center-of-mass coordinate of the positronium atom [Eqs. (13) and (14)]. Note that the matrix element (47) is local (diagonal in $\vec{r}$) in this representation, in spite of the fact that the finite size and structure of positronium are taken into account. The doubly renormalized matrix element $(\vec{r},\vec{r}_{ep},\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)''$ for decomposition of positronium into a positron and electron [the $\hat{p}^\dagger\hat{e}^\dagger\hat{\psi}_\nu$ term in (44)] is defined as follows. First, recalling that $x=(\vec{r}_p,\sigma_p)$ and $y=(\vec{r}_e,\sigma_e)$, one finds for the Fourier transform of the bare matrix element $(xy\mid V_{\mathrm{prot}}\mid\vec{k}\nu)$:

$$(xy\mid V_{\mathrm{prot}}\mid\vec{r}\nu)=(2\pi)^{-3/2}\int d\vec{k}\,e^{-i\vec{k}\cdot\vec{r}}(xy\mid V_{\mathrm{prot}}\mid\vec{k}\nu)=\delta(\vec{r}-\tfrac{1}{2}\vec{r}_e-\tfrac{1}{2}\vec{r}_p)\left[\frac{1}{r_p}-\frac{1}{r_e}\right]u_\nu(\vec{r}_{ep},\sigma_p,\sigma_e)\ , \tag{48}$$

which is again diagonal in the center-of-mass coordinate. Introducing $\vec{r}_{\mathrm{c.m.}}=(\frac{1}{2})(\vec{r}_e+\vec{r}_p)$ and $\vec{r}_{ep}=\vec{r}_e-\vec{r}_p$ as new integration variables instead of $\vec{r}_p$ and $\vec{r}_e$ and performing the trivial $\vec{r}_{\mathrm{c.m.}}$ integration, one obtains the expression (44) for the $\hat{p}^\dagger\hat{e}^\dagger\hat{\psi}_\nu$ term, in which the matrix element $(\ )''$ is defined by successive renormalizations (orthogonalizations to positronium and to bound hydrogen electrons) as follows:

$$\begin{aligned}
&(\vec{r},\vec{r}_{ep},\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)=\left[\frac{1}{|\vec{r}-\frac{1}{2}\vec{r}_{ep}|}-\frac{1}{|\vec{r}+\frac{1}{2}\vec{r}_{ep}|}\right]u_\nu(\vec{r}_{ep},\sigma_p,\sigma_e)\ ,\\
&(\vec{r},\vec{r}_{ep},\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)'=(\vec{r},\vec{r}_{ep},\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)-\int d\vec{r}'_{ep}\,\Delta_{\mathrm{Ps}}(\vec{r}_{ep},\vec{r}'_{ep};\sigma_p,\sigma_e)(\vec{r},\vec{r}'_{ep},\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)\ ,\\
&(\vec{r}_p\sigma_p,\vec{r}_e\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)''=\delta(\vec{r}-\tfrac{1}{2}\vec{r}_e-\tfrac{1}{2}\vec{r}_p)(\vec{r},\vec{r}_{ep},\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)'\\
&\qquad\qquad -8\Delta_e(\vec{r}_e,2\vec{r}-\vec{r}_p)(\vec{r},2\vec{r}-2\vec{r}_p,\sigma_p,\sigma_e\mid V_{\mathrm{prot}}\mid\vec{r}\nu)'\ .
\end{aligned} \tag{49}$$

Here the positronium bound-state kernel reduced to the relative wave functions u_ν [Eq. (13)] is found (Appendix D) to be

$$\Delta_{\mathrm{Ps}}(\vec{r}_{ep},\vec{r}'_{ep};\sigma_p,\sigma_e)=\sum_\nu u_\nu(\vec{r}_{ep},\sigma_p,\sigma_e)\times u_\nu^*(\vec{r}'_{ep},\sigma_p,\sigma_e)\ , \tag{50}$$

where use has been made of the fact that the full kernel (B23) is diagonal not only in the center-of-mass coordinate $\frac{1}{2}(\vec{r}_p+\vec{r}_e)$, but also in the positron and electron spin variables if spin-spin and spin-orbit interactions are negligible as assumed in (26). Both the unrenormalized and singly renormalized matrix elements are diagonal in the center-of-mass coordinate, but the subtraction term in the doubly renormalized matrix element $(\ )''$ involving the hydrogen bound-state kernel Δ_e is not, since the hydrogen bound orbitals $\varphi_{\nu e}$ are localized relative to the origin (position of the proton). The hydrogen bound-state kernel (32) is diagonal in spin, again assuming spin-spin and spin-orbit interactions negligible:

$$\Delta_e(y,y')=\Delta_e(r_e\sigma_e,r'_e\sigma'_e)=\delta_{\sigma_e\sigma'_e}\Delta_e(r_e,r'_e)\ ,$$
$$\Delta_e(r_e,r'_e)=\sum_\nu \varphi_{\nu e}(r_e\sigma_e)\varphi^*_{\nu e}(r'_e\sigma_e)\ . \tag{51}$$

The diagonality factor $\delta_{\sigma_e\sigma'_e}$ arises because each $\varphi_{\nu e}$ is an electron-spin z-component eigenstate, hence nonzero only for one value of σ_e, either $\sigma_e=\uparrow$ or $\sigma_e=\downarrow$. Then $\varphi_{\nu e}(\vec{r}_e\sigma_e)\varphi^*_{\nu e}(\vec{r}_e{}'\sigma'_e)$ is nonzero only if $\sigma_e=\sigma'_e$; the sum defining $\Delta_e(\vec{r}_e,\vec{r}_e{}')$ is not only diagonal in spin, but in fact spin independent.

The $\hat{p}^\dagger\hat{e}^\dagger_\nu\hat{\psi}_{\nu'}$ term in (44) is obtained by a similar derivation, leading to the following expression for the matrix element:

$$(\vec{r}_p\sigma_p,\nu\mid V_{\rm prot}\mid\vec{r}\nu')'=8(2\pi)^{-3/2}\sum_{\sigma_e}\varphi^*_{\nu e}(2\vec{r}-\vec{r}_p,\sigma_e)(\vec{r},2\vec{r}-2\vec{r}_p,\sigma_p,\sigma_e\mid V_{\rm prot}\mid\vec{r}\nu')'\ , \tag{52}$$

where the singly renormalized matrix element $(\vec{r},\vec{r}_{ep},\sigma_p,\sigma_e\mid V_{\rm prot}\mid\vec{r}\nu')'$ is defined by (49), and the $\vec{r}_e$ integration over a δ function factor $\delta(\vec{r}-\frac{1}{2}\vec{r}_e-\frac{1}{2}\vec{r}_p)$ has been performed, leading to the factor of 2 and the replacement $\vec{r}_e=2\vec{r}-\vec{r}_p$ and hence $\vec{r}_{ep}=2\vec{r}-2\vec{r}_p$, as in the subtraction term in the last Eq. (49).

The fact that all of the terms in $\hat{H}_0$ (and most of those in $\hat{V}$) have simple and obvious physical interpretations can be regarded as further evidence for the utility and physical relevance of the canonical transformation (16); (44) is an exact expression for the transformed Hamiltonian (19) on the one-positron one-electron subspace.

VI. CONSTRAINTS

In the same representation in which the Fock-Tani Hamiltonian (34) or (44) acts, the constraints (18) become

$$\hat{N}'_a\mid\ )=\hat{N}'_{\rm Ps}\mid\ )=0\ , \tag{53}$$

where $\mid\ )=\hat{U}^{-1}\mid\rangle$ and

$$\hat{N}'_a=\hat{U}^{-1}\hat{N}_a\hat{U}\ ,\quad \hat{N}'_{\rm Ps}=\hat{U}^{-1}\hat{N}_{\rm Ps}\hat{U} \tag{54}$$

with $\hat{N}_a$ and $\hat{N}_{\rm Ps}$ given by (19) and $\hat{U}$ by (16). Noting that the $\hat{e}_\nu$ commute with $\hat{F}_{\rm Ps}$, one has by (16)

$$\hat{N}'_a=\hat{U}_e^{-1}\hat{N}_a\hat{U}_e\ ,$$

which is easily evaluated (Appendix C) to give

$$\hat{N}'_a=\sum_\nu\hat{A}^\dagger_{\nu e}\hat{A}_{\nu e}=\int dy\,dy'\hat{e}^\dagger(y)\Delta_e(y,y')\hat{e}(y')\ . \tag{55}$$

$\hat{N}_{\rm Ps'}$ must be evaluated in two steps, as in (20). By (B9),

$$\hat{U}_{\rm Ps}^{-1}(\hat{N}_p+\hat{N}_{\rm Ps})\hat{U}_{\rm Ps}=\hat{N}_p+\hat{N}_{\rm Ps} \tag{56}$$

and hence

$$\hat{U}_{\rm Ps}^{-1}\hat{N}_{\rm Ps}\hat{U}_{\rm Ps}=\hat{N}_{\rm Ps}+\hat{N}_p-\hat{U}_{\rm Ps}^{-1}\hat{N}_p\hat{U}_{\rm Ps}\ . \tag{57}$$

Then transforming by $\hat{U}_e$ as in (20) and noting that $\hat{U}_e$ commutes with both $\hat{N}_p$ and $\hat{N}_{\rm Ps}$ [Eq. (33)], one has

$$\hat{N}'_{\rm Ps}=\hat{N}_{\rm Ps}+\hat{N}_p-\hat{N}'_p\ , \tag{58}$$

which reduces the evaluation of $\hat{N}'_{\rm Ps}$ to that of $\hat{N}'_p$. To evaluate the latter operator, note from (B8) and (1) that $\hat{N}_p$ can be obtained from $\hat{H}_F$ be replacing $H_p(x)$ by the unit operator and $H_e(y)$ and $V_{pe}(xy)$ by zero. This corresponds to replacing $T_p(x)$ by the unit operator, and $T_e(y)$ and all potential-energy terms by zero in the various contributions to (34) or (44). In this way one finds $\hat{N}'_p$, and hence, in the notation of (44), the following expression for $\hat{N}'_{\rm Ps}$:

$$\begin{aligned}\hat{N}'_{\rm Ps}=&\int dx\,dy\,dx'dy'\hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy\mid N'_{\rm Ps}\mid x'y')\hat{e}(y')\hat{p}(x')\\&+\sum_\nu\int dx\,dy\,dx'[\hat{p}^\dagger(x)\hat{e}^\dagger(y)(xy\mid N'_{\rm Ps}\mid x'\nu)\hat{e}_\nu\hat{p}(x')+\text{H.c.}]\\&+\sum_{\nu\nu'}\int dx\,dx'\hat{p}^\dagger(x)\hat{e}^\dagger_\nu(x\nu\mid N'_{\rm Ps}\mid x'\nu')\hat{e}_{\nu'}\hat{p}(x')\ .\end{aligned} \tag{59}$$

Here

$$(xy \mid N'_{\mathrm{Ps}} \mid x'y') = \Delta_{\mathrm{Ps}}(xy,x'y') - \int \Delta_e(y,y_1)\Delta_{\mathrm{Ps}}(xy_1,x'y')dy_1 - \int \Delta_{\mathrm{Ps}}(xy,x'y_1)\Delta_e(y_1,y')dy_1$$
$$+ \int \Delta_e(y,y_1)\Delta_{\mathrm{Ps}}(xy_1,x'y_2)\Delta_e(y_2,y')dy_1 dy_2 ,$$
$$(xy \mid N'_{\mathrm{Ps}} \mid x'\nu) = \int [\Delta_{\mathrm{Ps}}(xy,x'y') - \int \Delta_e(y,y'')\Delta_{\mathrm{Ps}}(xy'',x'y')dy'']\varphi_{\nu e}(y')dy' , \tag{60}$$
$$(x\nu \mid N'_{\mathrm{Ps}} \mid x'\nu') = \int \varphi^*_{\nu e}(y)\Delta_{\mathrm{Ps}}(xy,x'y')\varphi_{\nu' e}(y')dy\,dy' .$$

The expression (55) for $\hat{N}'_a$ is exact on the whole Fock-Tani state space, and that for $\hat{N}'_{\mathrm{Ps}}$ is exact on the one positron, one electron subspace relevant to the positron-hydrogen scattering problem. The way in which the constraints (53) are satisfied is discussed in the following section.

VII. ASYMPTOTIC STATES AND S MATRIX

The unperturbed states representing a free positron with wave vector k and spin z component σ_p, plus a free hydrogen atom in its νth bound state, are given in this representation by[7]

$$| \vec{k}\sigma_p,\nu) = (2\pi)^{-3/2} \int d\vec{r}_p e^{-i\vec{k}\cdot r_p} \hat{p}^\dagger(\vec{r}_p\sigma_p)\hat{e}^\dagger_\nu \mid 0\rangle \tag{61}$$

and are eigenstates of $\hat{H}_0$ [Eq. (44)] with eigenvalues $\frac{1}{2}\vec{k}^2+\epsilon_{\nu e}$. The corresponding in and out states $| \vec{k}\sigma_p,\nu)^{\pm}$ are given by the following expression from the formal theory of collisions:

$$| \vec{k}\sigma_p,\nu)^{\pm} = \pm \lim_{\eta\to 0+} i\eta(\tfrac{1}{2}\vec{k}^2+\epsilon_{\nu e}-\hat{H}\pm i\eta)^{-1} \times | \vec{k}\sigma_p,\nu) \tag{62}$$

and the S-matrix elements for elastic and inelastic positron-hydrogen scattering are

$$S(\vec{k}\sigma_p,\nu;\vec{k}'\sigma'_p,\nu') = {}^-(\vec{k}\sigma_p,\nu \mid k'\sigma_p,\nu')^+\delta_{\sigma_p\sigma'_p} . \tag{63}$$

The constraints (53) need not be enforced in computing the S-matrix elements. The reason is that the constraints are constants of the motion,

$$[\hat{N}'_a,\hat{H}] = [\hat{N}'_{\mathrm{Ps}},\hat{H}] = 0 , \tag{64}$$

since $\hat{N}_a$ and $\hat{N}_{\mathrm{Ps}}$ commute with the original Fock Hamiltonian $\hat{H}_F$ [see Eqs. (1), (19), and (12)]. Hence if the asymptotic unperturbed states $| \vec{k}\sigma_p,\nu)$ satisfy the constraints (53), it will follow from (62) that the $| \vec{k}\sigma_p,\nu)^{\pm}$ will also. It is shown in Appendix E that the asymptotic unperturbed states will indeed satisfy the constraints in the usual limit of wave packets localized infinitely far from the scatterer (here, the H atom). This is the usual limiting argument used to justify use of bare plane waves in defining the $| \vec{k}\sigma_p,\nu)$. The new point here is that this standard argument is sufficient to justify dropping the constraints (53) when calculating S-matrix elements in this new representation. It is not difficult to show that the same argument also applies to the asymptotic final states $| \vec{k}_p\sigma_p,\vec{k}_e\sigma_e)$ for reactive positron-hydrogen scattering, the corresponding out states $| \vec{k}_p\sigma_p,\vec{k}_e\sigma_e)^-$, and the resultant reactive S-matrix elements

$$S(\vec{k}_p\sigma_p,\vec{k}_e\sigma_e;\vec{k}'\sigma'_p,\nu) = {}^-(\vec{k}_p\sigma_p,\vec{k}_e\sigma_e \mid \vec{k}'\sigma_p,\nu)^+\delta_{\sigma_p\sigma'_p} . \tag{65}$$

This section will be concluded with a simple illustrative application of the new representation, namely, the lowest-order approximation to the process

$$e^+(\vec{k})+H(\nu_i)\to e^+(\vec{k}')+H(\nu_f) . \tag{66}$$

Cross sections for (66) and related processes have been extensively studied in the literature and we refer elsewhere for more conventional quantum-mechanical treatments.[23–25] The S matrix of (66) can be decomposed according to

$$S(\vec{k}'\sigma'_p,\nu_f;\vec{k}\sigma_p,\nu_i) = \delta(\vec{k}'-\vec{k})\delta_{\sigma'_p\sigma_p} - 2\pi i\delta(E-E')T(\vec{k}'\sigma'_p,\nu_f;\vec{k}\sigma_p,\nu_i) \tag{67}$$

with the second term on the rhs of (67) representing the T matrix for (66). To lowest order in the interaction ($T\approx T_1$) this becomes

$$T_1(\vec{k}'\sigma'_p,\nu_f;\vec{k}\sigma_p,\nu_i) = (\vec{k}'\sigma'_p,\nu_f \mid V \mid \vec{k}\sigma_p,\nu_i) \tag{68}$$

with V the potential responsible for the transition, explicitly given by (44), and $|\vec{k}\sigma_p,\nu)$ the noninteracting states of the theory, represented by (61). By using (44) in (68) and "pairing" creation and annihilation operators of the same kind, it is immediate to verify that T_1 reduces to

$$T_1(\vec{k}'\sigma_p',\nu_f;\vec{k}\sigma_p,\nu_i)=(2\pi)^{-3}\int d\vec{r}_p d\vec{r}_p' e^{-i\vec{k}'\cdot\vec{r}_p'}(x\nu_f\,|\,H_{pe}\,|\,x'\nu_i)' e^{i\vec{k}\cdot\vec{r}_p} \quad . \tag{69}$$

From (42) and (27) it readily follows that

$$\begin{aligned} T_1(\vec{k}'\sigma_p',\nu_f;\vec{k}\sigma_p,\nu_i)=(2\pi)^{-3}\int d\vec{r}_p d\vec{r}_p' dy\,dy' e^{-i\vec{k}'\cdot\vec{r}_p'}\varphi^*_{\nu_f e}(y) \\ \times\Big[V_{pe}(xy)\delta(x-x')\delta(y-y')-\sum_\alpha \epsilon_\alpha \varphi_{\alpha\mathrm{Ps}}(xy)\varphi^*_{\alpha\,\mathrm{Ps}}(x'y') \\ +(xy\,|\,V_{\mathrm{prot}}\,|\,x'y')'\Big]\varphi_{\nu_i e}(y')e^{i\vec{k}\cdot\vec{r}_p} \end{aligned} \tag{70}$$

with all the quantities being defined in Sec. V. The first term within large parentheses represents the conventional first Born contribution to the cross section. The remaining two terms represent corrections characteristic of the present formalism, corresponding to the binding of the e^+-e^- pair in positronium and to the screening of the charge of the proton, due to the Δ_{Ps} kernel, respectively. Even in lowest approximation, therefore, the present theory brings into the picture terms absent from a conventional quantum-mechanical treatment.

VIII. DISCUSSION

A new representation for low-energy positron-hydrogen scattering has been derived by starting with the standard Fock representation and carrying out a sequence of two canonical transformations: one to introduce a field operator for bound positronium, the other to introduce one for the bound atomic electron. The physical interpretations of the various terms in the transformed Hamiltonian have been discussed; these terms correspond directly with the various possible scattering and reaction channels, and include the effects of bound-state-continuum orthogonality in the matrix elements. This representation is expected to be useful for inclusion of the intermediate-state positronium channel in the standard many-body Green's-function approach.[1–5] Calculations using this representation will be described in subsequent publications.

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APPENDIX A: GRADED DIRECT PRODUCT CONSTRUCTION OF THE IDEAL STATE SPACE

Let $\mathscr{F}$ be the original electron-positron Fock space on which Eqs. (3), (6), and (9) are valid, with vacuum denoted by $|0,\mathscr{F}\rangle$. Let $\mathscr{B}$ be a completely independent Fock space on which the $\hat{\psi}_\alpha$, $\hat{\psi}^\dagger_\alpha$, $\hat{e}_\nu$, $\hat{e}^\dagger_\nu$ act, and on which

$$\begin{aligned} &[\hat{e}_\nu,\hat{e}_{\nu'}]_+=0,\quad [\hat{e}_\nu,\hat{e}^\dagger_{\nu'}]_+=\delta_{\nu\nu'}\,, \\ &[\hat{\psi}_\alpha,\hat{\psi}_\beta]_-=0,\quad [\hat{\psi}_\alpha,\hat{\psi}^\dagger_\beta]_-=\delta_{\alpha\beta}\,, \\ &[\hat{e}_\nu,\hat{\psi}_\alpha]_-=[\hat{e}_\nu,\hat{\psi}^\dagger_\alpha]_-=0\,. \end{aligned} \tag{A1}$$

Denote the vacuum of $\mathscr{B}$ by $|0,\mathscr{B}\rangle$. We want to combine $\mathscr{F}$ and $\mathscr{B}$ so as to produce an enlarged state space $\mathscr{I}$ on which the normal commutation relations[10] (3), (6), (9), and (12) may all be consistently imposed.

As a preliminary, recall the definition of the direct product. Let $|\psi(\mathscr{F})\rangle$, $\hat{F}(\mathscr{F})$ be any state and operator on $\mathscr{F}$, and let $|\psi(\mathscr{B})\rangle$, $\hat{B}(\mathscr{B})$ be any on $\mathscr{B}$. The direct product state

$$|\psi(\mathscr{F})\psi(\mathscr{B})\rangle\equiv|\psi(\mathscr{F})\rangle\otimes|\psi(\mathscr{B})\rangle$$

is defined implicitly by the requirement that it is bilinear in $|\psi(\mathscr{F})\rangle$ and $|\psi(\mathscr{B})\rangle$, by the inner product rule

$$\langle \psi(\mathscr{F})\psi(\mathscr{B}) \mid \psi'(\mathscr{F})\psi'(\mathscr{B})\rangle \equiv \langle \psi(\mathscr{F}) \mid \psi'(\mathscr{F})\rangle\langle \psi(\mathscr{B}) \mid \psi'(\mathscr{B})\rangle , \quad \text{(A2)}$$

and by the definition of direct product operators $\hat{F}(\mathscr{F})\otimes\hat{B}(\mathscr{B})$, which act, by definition, according to the rule

$$[\hat{F}(\mathscr{F})\otimes\hat{B}(\mathscr{B})] \mid \psi(\mathscr{F})\psi(\mathscr{B})\rangle \equiv [\hat{F}(\mathscr{F}) \mid \psi(\mathscr{F})\rangle]\otimes[\hat{B}(\mathscr{B}) \mid \psi(\mathscr{B})\rangle] . \quad (A3)$$

The direct product space $\mathscr{F}\otimes\mathscr{B}$ is spanned by all linear combinations $\sum_{ij}c_{ij} \mid \psi_i(\mathscr{F})\psi_j(\mathscr{B})\rangle$, and the definition (A3) is extended linearly to such linear combinations.[26] An important corollary of (A3) is that the vacuum state $\mid 0\rangle$ of $\mathscr{F}\otimes\mathscr{B}$ is the direct product $\mid 0,\mathscr{F}\rangle\otimes\mid 0,\mathscr{B}\rangle$. It follows from (A3) that

$$[\hat{F}_1(\mathscr{F})\otimes\hat{B}_1(\mathscr{B})][\hat{F}_2(\mathscr{F})\otimes\hat{B}_2(\mathscr{B})] = [\hat{F}_1(\mathscr{F})\hat{F}_2(\mathscr{F})]\otimes[\hat{B}_1(\mathscr{B})\hat{B}_2(\mathscr{B})] . \quad (A4)$$

One is tempted to define the ideal state space $\mathscr{I}$ to be the direct product $\mathscr{F}\otimes\mathscr{B}$, with operators $\hat{F}(\mathscr{F})$ and $\hat{B}(\mathscr{B})$ extended to $\mathscr{I}$ in the usual way $\hat{F}(\mathscr{I})=\hat{F}(\mathscr{F})\otimes\hat{1}(\mathscr{B})$, $\hat{B}(\mathscr{I})=\hat{1}(\mathscr{F})\otimes\hat{B}(\mathscr{B})$, where $\hat{1}(\mathscr{F})$ and $\hat{1}(\mathscr{B})$ are the unit operators on $\mathscr{F}$ and $\mathscr{B}$, respectively. However, such a procedure fails in the present case because the product rule (A4) implies commutativity on $\mathscr{I}$, i.e. $[\hat{F}(\mathscr{I}), \hat{B}(\mathscr{I})]_-=0$. This disagrees with the *anti*commutation rules between $\hat{e}_\nu$, $\hat{e}_\nu{}^\dagger$ and the original positron and electron fields $\hat{p}(x)$, $\hat{p}^\dagger(x)$, $\hat{e}(y)$, and $\hat{e}^\dagger(y)$ [Eq. (12)]. Replacing these anticommutators by commutators results in abnormal commutation relations,[10] i.e., some *fermion* fields *commute* with others. This situation can be corrected by generalizing to a "graded direct product" $\mathscr{I}=\mathscr{F}\otimes_g\mathscr{B}$. This is done by introducing an appropriate phase operator $\hat{\Phi}(\mathscr{F})$ on $\mathscr{F}$, defined by

$$\hat{\Phi}(\mathscr{F})=\exp\left\{i\pi\left[\int dx\,\hat{p}^\dagger(x)\hat{p}(x) + \int dy\,\hat{e}^\dagger(y)\hat{e}(y)\right]\right\} \quad (A5)$$

involving the number operators for positrons and electrons. Then on $\mathscr{F}$ the positron and electron fields $\hat{p}(x)$, $\hat{p}^\dagger(x)$, $\hat{e}(y)$, and $\hat{e}^\dagger(y)$ all anticommute with $\hat{\Phi}(\mathscr{F})$. More generally, *odd* polynomials in these fields *anti*commute with Φ whereas *even* polynomials *commute* with $\hat{\Phi}$. The graded direct product space $\mathscr{I}=\mathscr{F}\otimes_g\mathscr{B}$ is then defined by retaining the usual direct product rules (A2)–(A4), but modifying the rules for extension of some of the operators from $\mathscr{B}$ to $\mathscr{I}$. Specifically, we define

$$\hat{F}(\mathscr{I})\equiv\hat{F}(\mathscr{F})\otimes\hat{1}(\mathscr{B}) \quad (A6)$$

as usual for all operators on $\mathscr{F}$, but the rules for extension of operators on $\mathscr{B}$ to $\mathscr{I}$ are changed to

$$\begin{aligned}
\hat{e}_\nu(\mathscr{I})&\equiv\hat{\Phi}(\mathscr{F})\otimes\hat{e}_\nu(\mathscr{B}) ,\\
\hat{e}_\nu^\dagger(\mathscr{I})&\equiv\hat{\Phi}(\mathscr{F})\otimes\hat{e}_\nu^\dagger(\mathscr{B}) ,\\
\hat{\psi}_\alpha(\mathscr{I})&\equiv\hat{1}(\mathscr{F})\otimes\hat{\psi}_\alpha(\mathscr{B}) ,\\
\hat{\psi}_\alpha^\dagger(\mathscr{I})&\equiv\hat{1}(\mathscr{F})\otimes\hat{\psi}_\alpha^\dagger(\mathscr{B}) .
\end{aligned} \quad (A7)$$

Note that this implies that polynomials in the $\hat{e}_\nu$, $\hat{e}_\nu^\dagger$, $\hat{\psi}_\alpha$, and $\hat{\psi}_\alpha^\dagger$ are extended to $\mathscr{I}$ by direct multiplying terms *odd* in $\hat{e}_\nu$, $\hat{e}_\nu^\dagger$ by $\hat{\Phi}(\mathscr{F})$, whereas terms *even* in $\hat{e}_\nu$, $\hat{e}_\nu^\dagger$ are direct multiplied by $\hat{1}(\mathscr{F})$ as usual, since $\hat{\Phi}^2=1$. In connection with the second Eq. (A7), note that $\hat{\Phi}^\dagger=\hat{\Phi}^{-1}=\hat{\Phi}$. It is then easy to verify that the normal commutation rules (3), (6), (9), and (12) are all satisfied. An alternative procedure would be to first extend all operators (including $\hat{\Phi}$) from $\mathscr{F}$ and $\mathscr{B}$ to $\mathscr{I}$ in the usual way using only $\hat{1}(\mathscr{F})$ and $\hat{1}(\mathscr{B})$ in the direct products, and then "correcting" the resultant $\hat{e}_\nu$ and $\hat{e}_\nu^\dagger$ operators on $\mathscr{I}$ by multiplication by $\hat{\Phi}(\mathscr{I})$. This is the method of the Klein transformation.[10]

APPENDIX B: EVALUATION OF POSITRONIUM TANI TRANSFORMATION

Procedures for evaluation of $\hat{U}_{\rm Ps}^{-1}\hat{H}_F\hat{U}_{\rm Ps}$ have been described previously[6,27] in a different connection. However, the methods used there emphasized the infinite series aspect of the transformed Hamiltonian, a complication occurring in applications to macroscopic systems of arbitrarily many composite particles. In the present case only one positronium atom can form since there is only one positron. Then a simpler and more transparent derivation, which will be presented herein, leads to an exact and explicit expression with no infinite series.

The method which will be used is based on an equation of motion and operator-basis-expansion method[27] simplified by the restriction to the one-positron subspace. Let $\hat{A}$ denote any of the operators $\hat{e}^\dagger(y)\hat{e}(y')$, $\hat{p}^\dagger(x)\hat{p}(x')$, etc. whose transforms $\hat{U}_{\rm Ps}^{-1}\hat{A}\hat{U}_{\rm Ps}$ we wish to evaluate. In this connection,

it is expedient to rewrite

$$\hat{e}^{\dagger}(y)H_e(y)\hat{e}(y)=\lim_{y'\to y}\{H_e(y')[\hat{e}^{\dagger}(y)\hat{e}(y')]\} \tag{B1}$$

and similarly for $\hat{p}^{\dagger}(x)H_p(x)\hat{p}(x)$, in view of the differentiation operation in $H_e(y)$ and $H_p(x)$, Eq. (2). Define

$$\hat{A}(t)=e^{-t\hat{F}_{\rm Ps}}\hat{A}e^{t\hat{F}_{\rm Ps}}\ , \tag{B2}$$

where $\hat{F}_{\rm Ps}$ is given in Eq. (16). Then $\hat{A}(t)$ satisfies the "equation of motion"

$$\frac{d\hat{A}(t)}{dt}=[\hat{A}(t),\hat{F}_{\rm Ps}]_-\ , \tag{B3}$$

which is to be solved subject to the "initial" condition $\hat{A}(0)=\hat{A}$ to yield the transform

$$\hat{A}\left[\frac{\pi}{2}\right]=\hat{U}_{\rm Ps}^{-1}\hat{A}\hat{U}_{\rm Ps}\ . \tag{B4}$$

Define an "operator basis" $\{\hat{B}_i\}$ whose linearly independent[28] elements $\hat{B}_i$ are all of the distinct normally ordered products of creation operators $\hat{p}^{\dagger}(x)$, $\hat{e}^{\dagger}(y)$, $\hat{\psi}_{\alpha}{}^{\dagger}$ and annihilation operators $\hat{p}(x)$, $\hat{e}(y)$, $\hat{\psi}_{\alpha}$. Each i is a double index: $i=(\mathscr{S}_{\rm out},\mathscr{S}_{\rm in})$, where $\mathscr{S}_{\rm in}$ is the set of labels of the incoming particles (annihilation operators) and $\mathscr{S}_{\rm out}$ that for the outgoing particles (creation operators). This doubling of indices is familiar[29] in Liouvillian approaches to time-dependent quantum mechanics. $\hat{A}(t)$ can be expanded in terms of the basis $\{\hat{B}_i\}$:

$$\hat{A}(t)=\sum_i c_i(t)\hat{B}_i\ , \tag{B5}$$

where the $c_i(t)$ are c-number functions of t to be determined. Substitution into (B3) and equation of coefficients of the same basis element on both sides leads to coupled linear equations of motion for the $c_i(t)$,

$$\frac{dc_i(t)}{dt}=\sum_j c_j(t)d_{ji}\ , \tag{B6}$$

where (d_{ji}) is the "d matrix"[27] defined by

$$[\hat{B}_j,\hat{F}_{\rm Ps}]_-=\sum_i d_{ji}\hat{B}_i\ . \tag{B7}$$

As previously noted, each index i or j stands for a set of both incoming and outgoing particles; the d_{ji} are matrix elements of the commutation superoperator defined by (B7), just as is the Liouvillian tetradic.[29] The initial values $c_i(0)$ are to be chosen so that the initial condition $\hat{A}(0)=\hat{A}$ is satisfied. Equations (B6) have an obvious solution in terms of the exponential of the d matrix, but in practice other methods of solution are easier than exponentiation of the d matrix.

The set of $\hat{B}_i$ which enter into the expansion of a given $\hat{A}(t)$ can be severely truncated in a case such as that in which we are interested here, where all operators act only on a low-order subspace of the Fock space. To make this explicit, consider the positron and electron number operators

$$\begin{aligned}\hat{N}_p&=\int dx\,\hat{p}^{\dagger}(x)\hat{p}(x)\ ,\\ \hat{N}_e&=\int dy\,\hat{e}^{\dagger}(y)\hat{e}(y)\ ,\end{aligned} \tag{B8}$$

along with the number operator $\hat{N}_{ps}$ for ideal positronium atoms, Eq. (19). It is easy to show that

$$\begin{aligned}&[(\hat{N}_p+\hat{N}_{\rm Ps}),\hat{U}_{\rm Ps}]=0\ ,\\ &[(\hat{N}_e+\hat{N}_{\rm Ps}),\hat{U}_{\rm Ps}]=0\ .\end{aligned} \tag{B9}$$

The physical content of this is that the transformation conserves the total numbers of both positrons and electrons; in the Fock-Tani state space, $\hat{N}_p$ counts free positrons and $\hat{N}_{\rm Ps}$ counts bound ones (one in each positronium atom), and similarly, $\hat{N}_e$ counts free electrons and $\hat{N}_{\rm Ps}$ counts bound ones[30] (one bound in each positronium atom). Let $\mathscr{I}_{nm}$ be the subspace of the Fock-Tani state space $\mathscr{I}$ (Appendix A) containing n positrons and m electrons[30]:

$$\left.\begin{aligned}(\hat{N}_p+\hat{N}_{\rm Ps})\,|\,n,m\,\rangle&=n\,|\,n,m\,\rangle\\ (\hat{N}_e+\hat{N}_{\rm Ps})\,|\,n,m\,\rangle&=m\,|\,n,m\,\rangle\end{aligned}\right\}\ \text{if}\ \ |\,n,m\,\rangle\in\mathscr{I}_{nm}\ . \tag{B10}$$

We will eventually be interested only in $\mathscr{I}_{11}$, but it is useful at this point to be more general. Now suppose that the operator $\hat{A}$ annihilates $\mathscr{I}_{nm}$,

$$\hat{A}\mathscr{I}_{nm}=0 \tag{B11}$$

(in the sense that it annihilates every $|\,\psi\rangle\in\mathscr{I}_{nm}$) for some particular choices of n and m. Then for the same n and m one will also have

$$\hat{A}(t)\mathscr{I}_{nm}=0 \tag{B12}$$

as a consequence of (B2), (B9), and (B10). Then the only $\hat{B}_i$ which can enter in the expansion (B5) of $\hat{A}(t)$ are those which annihilate $\mathscr{I}_{nm}$. Further delimitation is provided by noticing that we are interested in Eq. (1) only in operators $\hat{A}$ which commute with both $\hat{N}_p+\hat{N}_{Ps}$ and $\hat{N}_e+\hat{N}_{Ps}$, and hence the same must be true of all the $\hat{B}_i$ occurring in the expansion of $\hat{A}(t)$. Finally, restriction to various one-positron, m-electron subspaces $\mathscr{I}_{1m}$ is introduced by deleting from the expansion of $\hat{A}(t)$ all

$\hat{B}_i$ which annihilate the relevant $\mathscr{S}_{1m}$. This is most efficiently done sequentially, first retaining only the terms which are nonzero on $\mathscr{S}_{10}$, then adding the additional terms which are zero on $\mathscr{S}_{10}$ but nonzero on $\mathscr{S}_{11}$ (without changing the previously obtained terms), etc.

To make this more concrete, consider the expansion of $\hat{p}^\dagger(x,t)\hat{p}(x',t)$. Noting that $\hat{p}^\dagger(x)\hat{p}(x')$ annihilates the $\mathscr{S}_{0m}$ for arbitrary m, one sees that the only terms which can occur in the expansion of $\hat{p}^\dagger(x,t)\hat{p}(x',t)$ restricted to $\mathscr{S}_{10}$ are the $\hat{p}^\dagger(x_1)\hat{p}(x_2)$. Thus (B5) reduces on $\mathscr{S}_{10}$ to

$$[\hat{p}^\dagger(x,t)\hat{p}(x',t)]_{10}=\int dx_1dx_2c(x;x'\,|\,x_1;x_2\,|\,t)\hat{p}^\dagger(x_1)\hat{p}(x_2) \tag{B13}$$

and (B6) to

$$\frac{dc(x;x'\,|\,x_1;x_2\,|\,t)}{dt}=\int dx_3dx_4c(x;x'\,|\,x_3;x_4\,|\,t)d(x_3;x_4\,|\,x_1;x_2)\,, \tag{B14}$$

which is to be solved subject to the initial condition

$$c(x;x'\,|\,x_1;x_2\,|\,0)=\delta(x-x_1)\delta(x'-x_2)\,. \tag{B15}$$

Upon evaluating commutators (B7) one finds that all of the d-matrix elements d_{ji} with column $i=(x_1;x_2)$ [basis elements $\hat{B}_i=\hat{p}^\dagger(x_1)\hat{p}(x_2)$ in (B7)] are zero. Hence the derivative (B14) vanishes and

$$c(x;x'\,|\,x_1;x_2\,|\,t)=\delta(x-x_1)\delta(x'-x_2) \tag{B16}$$

implying

$$[\hat{p}^\dagger(x,t)\hat{p}(x',t)]_{10}=\hat{p}^\dagger(x)\hat{p}(x')\,. \tag{B17}$$

To extend this to $\mathscr{S}_{11}$, one must add terms proportional to those basis elements vanishing on $\mathscr{S}_{10}$ but not on $\mathscr{S}_{11}$. Choosing these terms in accordance with the aforementioned criteria, one finds

$$\begin{aligned}[\hat{p}^\dagger(x,t)\hat{p}(x',t)]_{11}=\hat{p}^\dagger(x)\hat{p}(x')&+\sum_{\alpha\beta}c(x;x'\,|\,\alpha;\beta\,|\,t)\hat{\psi}_\alpha{}^\dagger\hat{\psi}_\beta\\&+\sum_\alpha\int dx_1dy_1[c(x;x'\,|\,x_1y_1;\alpha\,|\,t)\hat{p}^\dagger(x_1)\hat{e}^\dagger(y_1)\hat{\psi}_\alpha+c(x;x'\,|\,\alpha;x_1y_1\,|\,t)\hat{\psi}_\alpha^\dagger\hat{e}(y_1)\hat{p}(x_1)]\\&+\int dx_1dy_1dx_2dy_2c(x;x'\,|\,x_1y_1;x_2y_2\,|\,t)\hat{p}^\dagger(x_1)\hat{e}^\dagger(y_1)\hat{e}(y_2)\hat{p}(x_2)\,.\end{aligned} \tag{B18}$$

Note, for example, that terms $\hat{e}^\dagger(y_1)\hat{e}(y_2)$ cannot occur in (B18) because $\hat{p}^\dagger\hat{p}$ annihilates $\mathscr{S}_{01}$. The relevant differential equations (B6) are then

$$\begin{aligned}\frac{dc(x;x'\,|\,i\,|\,t)}{dt}=d(x;x'\,|\,i)&+\sum_{\alpha\beta}c(x;x'\,|\,\alpha;\beta\,|\,t)d(\alpha;\beta\,|\,i)\\&+\sum_\alpha\int dx_1dx_2c(x;x'\,|\,x_1y_1;\alpha\,|\,t)d(x_1y_1;\alpha\,|\,i)\\&+\sum_\alpha\int dx_1dx_2c(x;x'\,|\,\alpha;x_1y_1\,|\,t)d(\alpha;x_1y_1\,|\,i)\\&+\int dx_1dy_1dx_2dy_2c(x;x'\,|\,x_1y_1;x_2y_2\,|\,t)d(x_1y_1;x_2y_2\,|\,i)\,,\end{aligned} \tag{B19}$$

where i ranges over the labels of the new basis elements, namely, $i=(\alpha;\beta)$, $i=(x_1y_1;\alpha)$, $i=(\alpha;x_1y_1)$, and $i=(x_1y_1;x_2y_2)$. The inhomogeneous term $d(x;x'\,|\,i)$ arises from (B16) and (B6). The necessary d-matrix elements in (B19) can be found either by direct evaluation of commutators (B7), or more quickly by change of notation in the previous results[27] for atomic hydrogen [proton changed to positron, and sign of the matrix

elements changed to correspond to the sign convention in the definition of $\hat{F}_{\mathrm{Ps}}$, Eq. (16)]. The results are

$$
\begin{aligned}
&d(x;x'\,|\,\alpha;\beta)=d(x;x'\,|\,x_1y_1;x_2y_2)=0\,,\\
&d(x;x'\,|\,x_1y_1;\alpha)=\varphi_{\alpha\mathrm{Ps}}(x'y_1)\delta(x-x_1)\,,\\
&d(x;x'\,|\,\alpha;x_1y_1)=\varphi^*_{\alpha\mathrm{Ps}}(xy_1)\delta(x'-x_1)\,,\\
&d(\alpha;\beta\,|\,\gamma;\delta)=d(\alpha;\beta\,|\,x_1y_1;x_2y_2)=0\,,\\
&d(\alpha;\beta\,|\,x_1y_1;\gamma)=-\varphi_{\alpha\mathrm{Ps}}(x_1y_1)\delta_{\beta\gamma}\,,\\
&d(\alpha;\beta\,|\,\gamma;x_1y_1)=-\varphi^*_{\alpha\mathrm{Ps}}(x_1y_1)\delta_{\alpha\gamma}\,,\\
&d(x_1y_1;\alpha\,|\,\beta;\gamma)=\varphi^*_{\beta\mathrm{Ps}}(x_1y_1)\delta_{\alpha\gamma}\,,\\
&d(x_2y_2;\alpha\,|\,x_1y_1;\beta)=d(x_2y_2;\alpha\,|\,\beta;x_1y_1)=0\,,\\
&d(x_2y_2;\alpha\,|\,x_1y_1;x_3y_3)=-\varphi^*_{\alpha\mathrm{Ps}}(x_3y_3)\delta(x_2-x_1)\delta(y_2-y_1)\,,\\
&d(\alpha;x_1y_1\,|\,\beta;\gamma)=\varphi_{\gamma\mathrm{Ps}}(x_1y_1)\delta_{\alpha\beta}\,,\\
&d(\alpha;x_2y_2\,|\,x_1y_1;\beta)=d(\alpha;x_2y_2\,|\,\beta;x_1y_1)=0\,,\\
&d(\alpha;x_2y_2\,|\,x_1y_1;x_3y_3)=-\varphi_{\alpha\mathrm{Ps}}(x_1y_1)\delta(x_2-x_3)\delta(y_2-y_3)\,,\\
&d(x_1y_1;x_2y_2\,|\,\alpha;\beta)=d(x_3y_3;x_4y_4\,|\,x_1y_1;x_2y_2)=0\,,\\
&d(x_2y_2;x_3y_3\,|\,x_1y_1;\alpha)=\varphi_{\alpha\mathrm{Ps}}(x_3y_3)\delta(x_2-x_1)\delta(y_2-y_1)\,,\\
&d(x_2y_2;x_3y_3\,|\,\alpha;x_1y_1)=\varphi^*_{\alpha\mathrm{Ps}}(x_2y_2)\delta(x_3-x_1)\delta(y_3-y_1)\,.
\end{aligned}
\tag{B20}
$$

Thus the differential equations (B19) become

$$
\begin{aligned}
&\frac{dc(x;x'\,|\,\alpha;\beta\,|\,t)}{dt}=\int dx_1dy_1[\varphi^*_{\alpha\mathrm{Ps}}(x_1y_1)c(x;x'\,|\,x_1y_1;\beta\,|\,t)+\varphi_{\beta\mathrm{Ps}}(x_1y_1)c(x;x'\,|\,\alpha;x_1y_1\,|\,t)]\,,\\
&\frac{dc(x;x'\,|\,x_1y_1;\alpha\,|\,t)}{dt}=\varphi_{\alpha\mathrm{Ps}}(x'y_1)\delta(x-x_1)-\sum_{\beta}\varphi_{\beta\mathrm{Ps}}(x_1y_1)c(x;x'\,|\,\beta;\alpha\,|\,t)\\
&\qquad\qquad+\int dx_2dy_2\varphi_{\alpha\mathrm{Ps}}(x_2y_2)c(x;x'\,|\,x_1y_1;x_2y_2\,|\,t)\,,\\
&\frac{dc(x;x'\,|\,\alpha;x_1y_1\,|\,t)}{dt}=\varphi^*_{\alpha\mathrm{Ps}}(xy_1)\delta(x'-x_1)-\sum_{\beta}\varphi^*_{\beta\mathrm{Ps}}(x_1y_1)c(x;x'\,|\,\alpha;\beta\,|\,t)\\
&\qquad\qquad+\int dx_2dy_2\varphi^*_{\alpha\mathrm{Ps}}(x_2y_2)c(x;x'\,|\,x_2y_2;x_1y_1\,|\,t)\,,\\
&\frac{dc(x;x'\,|\,x_1y_1;x_2y_2\,|\,t)}{dt}=-\sum_{\alpha}[\varphi^*_{\alpha\mathrm{Ps}}(x_2y_2)c(x;x'\,|\,x_1y_1;\alpha\,|\,t)+\varphi_{\alpha\mathrm{Ps}}(x_1y_1)c(x;x'\,|\,\alpha;x_2y_2\,|\,t)\,.
\end{aligned}
\tag{B21}
$$

The solutions are

$$
\begin{aligned}
&c(x;x'\,|\,\alpha;\beta\,|\,t)=\int dy\,\varphi^*_{\alpha\mathrm{Ps}}(xy)\varphi_{\beta\mathrm{Ps}}(x'y)\sin^2t\,,\\
&c(x;x'\,|\,x_1y_1;\alpha\,|\,t)=\varphi_{\alpha\mathrm{Ps}}(x'y_1)\delta(x-x_1)\sin t-\int dy\,\Delta_{\mathrm{Ps}}(x_1y_1,xy)\varphi_{\alpha\mathrm{Ps}}(x'y)\sin t(1-\cos t)\,,\\
&c(x;x'\,|\,\alpha;x_1y_1\,|\,t)=\varphi^*_{\alpha\mathrm{Ps}}(xy_1)\delta(x'-x_1)\sin t-\int dy\,\varphi^*_{\alpha\mathrm{Ps}}(xy)\Delta_{\mathrm{Ps}}(x'y,x_1y_1)\sin t(1-\cos t)\,,\\
&c(x;x'\,|\,x_1y_1;x_2y_2\,|\,t)=-\Delta_{\mathrm{Ps}}(x_1y_1,xy_2)\delta(x'-x_2)(1-\cos t)-\Delta_{\mathrm{Ps}}(x'y_1,x_2y_2)\delta(x-x_1)(1-\cos t)\,,\\
&\qquad\qquad+\int dy\,\Delta_{\mathrm{Ps}}(x_1y_1,xy)\Delta_{\mathrm{Ps}}(x'y,x_2y_2)(1-\cos t)^2\,,
\end{aligned}
\tag{B22}
$$

where Δ_{Ps} is the positronium bound-state kernel

$$\Delta_{\mathrm{Ps}}(x_1y_1,x_2y_2)=\sum_{\alpha}\varphi_{\alpha\,\mathrm{Ps}}(x_1y_1)\varphi^{*}_{\alpha\,\mathrm{Ps}}(x_2y_2)\ . \tag{B23}$$

These vanish at $t=0$ as they must in order that $[\hat{p}^{\dagger}(x)\hat{p}(x')]_1$ reduce to $\hat{p}^{\dagger}(x)\hat{p}(x')$ at $t=0$, and it can be verified by direct substitution that they satisfy the differential equations (B21). This verification makes use of the identities

$$\begin{aligned}&\int\varphi^{*}_{\alpha\,\mathrm{Ps}}(x_1y_1)\Delta_{\mathrm{Ps}}(x_1y_1,x_2y_2)dx_1dy_1=\varphi^{*}_{\alpha\,\mathrm{Ps}}(x_2y_2)\ ,\\&\int\Delta_{\mathrm{Ps}}(x_1y_1,x_2y_2)\varphi_{\alpha\,\mathrm{Ps}}(x_2y_2)dx_2dy_2=\varphi_{\alpha\,\mathrm{Ps}}(x_1y_1)\ ,\end{aligned} \tag{B24}$$

which follow from orthonormality of the $\varphi_{\alpha\,\mathrm{Ps}}$. These solutions are found most efficiently by adaptation of the previously studied cases.[6,27] The expression for the transform of $\hat{p}^{\dagger}(x)\hat{p}(x')$ exact on $\mathscr{I}_{11}$ is then found by substitution of (B22) into (B18).

Let us next work out the expressions for the transforms of the other operators in (1) through terms exact on $\mathscr{I}_{11}$. Since these terms annihilate $\mathscr{I}_{10}$ one has

$$\begin{aligned}&[\hat{e}^{\dagger}(y,t)\hat{e}(y',t)]_{10}=0\ ,\\&[\hat{p}^{\dagger}(x,t)\hat{e}^{\dagger}(y,t)\hat{e}(y,t)\hat{p}(x,t)]_{10}=0\ .\end{aligned} \tag{B25}$$

The derivation of the expression for $\hat{e}^{\dagger}(y,t)\hat{e}(y',t)$ on $\mathscr{I}_{11}$ differs from that for $\hat{p}^{\dagger}(x,t)\hat{p}(x',t)$ only by some sign changes and interchanges of positron and electron arguments, so I shall only record the result:

$$\begin{aligned}[\hat{e}^{\dagger}(y,t)\hat{e}(y',t)]_{11}=\hat{e}^{\dagger}(y)\hat{e}(y')&+\sum_{\alpha\beta}c(y;y'\mid\alpha;\beta\mid t)\hat{\psi}^{\dagger}_{\alpha}\hat{\psi}_{\beta}\\&+\sum_{\alpha}\int dx_1dy_1[\,c(y;y'\mid x_1y_1;\alpha\mid t)\hat{p}^{\dagger}(x_1)\hat{e}^{\dagger}(y_1)\hat{\psi}_{\alpha}+c(y;y'\mid\alpha;x_1y_1\mid t)\hat{\psi}^{\dagger}_{\alpha}\hat{e}(y_1)\hat{p}(x_1)]\\&+\int dx_1dy_1dx_2dy_2c(y;y'\mid x_1y_1;x_2y_2\mid t)\hat{p}^{\dagger}(x_1)\hat{e}^{\dagger}(y_1)\hat{e}(y_2)\hat{p}(x_2)\end{aligned} \tag{B26}$$

with

$$\begin{aligned}c(y;y'\mid\alpha;\beta\mid t)&=\int dx\,\varphi^{*}_{\alpha\,\mathrm{Ps}}(xy)\varphi_{\beta\,\mathrm{Ps}}(xy')\sin^2t\ ,\\c(y;y'\mid x_1y_1;\alpha\mid t)&=\varphi_{\alpha\,\mathrm{Ps}}(x_1y')\delta(y-y_1)\sin t-\int dx\,\Delta_{\mathrm{Ps}}(x_1y_1,xy)\varphi_{\alpha\,\mathrm{Ps}}(xy')\sin t(1-\cos t)\ ,\\c(y;y'\mid\alpha;x_1y_1\mid t)&=\varphi^{*}_{\alpha\,\mathrm{Ps}}(x_1y)\delta(y'-y_1)\sin t\\&\quad-\int dx\,\varphi^{*}_{\alpha\,\mathrm{Ps}}(xy)\Delta_{\mathrm{Ps}}(xy',x_1y_1)\sin t(1-\cos t)\ ,\\c(y;y'\mid x_1y_1;x_2y_2\mid t)&=-\Delta_{\mathrm{Ps}}(x_1y_1,x_2y)\delta(y'-y_2)(1-\cos t)\\&\quad-\Delta_{\mathrm{Ps}}(x_1y',x_2y_2)\delta(y-y_1)(1-\cos t)\\&\quad+\int dx\,\Delta_{\mathrm{Ps}}(x_1y_1,xy)\Delta_{\mathrm{Ps}}(xy',x_2y_2)(1-\cos t)^2\ .\end{aligned} \tag{B27}$$

The $\mathscr{I}_{11}$ basis expansion of the transform of $\hat{p}^{\dagger}\hat{e}^{\dagger}\hat{e}\,\hat{p}$ is analogous to (B18) except that there is no $\hat{p}^{\dagger}\hat{p}$ term:

$$\begin{aligned}[\hat{p}^{\dagger}(x,t)\hat{e}^{\dagger}(y,t)\hat{e}(y,t)\hat{p}(x,t)]_{11}=&\sum_{\alpha\beta}c(xy;xy\mid\alpha;\beta\mid t)\hat{\psi}^{\dagger}_{\alpha}\hat{\psi}_{\beta}\\&+\sum_{\alpha}\int dx_1dy_1[\,c(xy;xy\mid x_1y_1;\alpha\mid t)\hat{p}^{\dagger}(x_1)\hat{e}^{\dagger}(y_1)\hat{\psi}_{\alpha}\\&\qquad+c(xy;xy\mid\alpha;x_1y_1\mid t)\hat{\psi}^{\dagger}_{\alpha}\hat{e}(y_1)\hat{p}(x_1)]\\&+\int dx_1dy_1dx_2dy_2c(xy;xy\mid x_1y_1;x_2y_2\mid t)\,\hat{p}^{\dagger}(x_1)\hat{e}^{\dagger}(y_1)\hat{e}(y_2)\hat{p}(x_2)\ .\end{aligned} \tag{B28}$$

The equations of motion analogous to (B19) are

$$\frac{dc(xy;xy\mid i\mid t)}{dt}=\sum_{\alpha\beta}c(xy;xy\mid\alpha;\beta\mid t)d(\alpha;\beta\mid i)+\sum_{\alpha}\int dx_1dy_1c(xy;xy\mid x_1y_1;\alpha\mid t)d(x_1y_1;\alpha\mid i)$$
$$+\sum_{\alpha}\int dx_1dy_1c(xy;xy\mid\alpha;x_1y_1\mid t)d(\alpha;x_1y_1\mid i)$$
$$+\int dx_1dy_1dx_2dy_2c(xy;xy\mid x_1y_1;x_2y_2\mid t)d(x_1y_1;x_2y_2\mid i)\ , \tag{B29}$$

where i ranges over the same operator basis elements as in (B19), and the $\mathscr{F}_{11}$-subspace d-matrix elements are also the same, Eq. (B20). There is no inhomogeneous term in (B29) since $\hat{p}^\dagger\hat{e}^\dagger\hat{e}\hat{p}$ vanishes on the lower subspaces. The solution subject to the initial condition

$$[\hat{p}^\dagger(x,0)\hat{e}^\dagger(y,0)\hat{e}(y,0)\hat{p}(x,0)]_{11}=\hat{p}^\dagger(x)\hat{e}^\dagger(y)\hat{e}(y)\hat{p}(x) \tag{B30}$$

is, not surprisingly, very similar to (B22):

$$c(xy;xy\mid\alpha;\beta\mid t)=\varphi^*_{\alpha\,\mathrm{Ps}}(xy)\varphi_{\beta\,\mathrm{Ps}}(xy)\sin^2t\ ,$$
$$c(xy;xy\mid x_1y_1;\alpha\mid t)=\varphi_{\alpha\,\mathrm{Ps}}(xy)\delta(x-x_1)\delta(y-y_1)\sin t$$
$$-\Delta_{\mathrm{Ps}}(x_1y_1,xy)\varphi_{\alpha\,\mathrm{Ps}}(xy)\sin t(1-\cos t)\ ,$$
$$c(xy;xy\mid\alpha;x_1y_1\mid t)=\varphi^*_{\alpha\,\mathrm{Ps}}(xy)\delta(x-x_1)\delta(y-y_1)\sin t$$
$$-\varphi^*_{\alpha\,\mathrm{Ps}}(xy)\Delta_{\mathrm{Ps}}(xy,x_1y_1)\sin t(1-\cos t)\ ,$$
$$c(xy;xy\mid x_1y_1',x_2y_2\mid t)=\delta(x-x_1)\delta(y-y_1)\delta(x-x_2)\delta(y-y_2)$$
$$-\Delta_{\mathrm{Ps}}(x_1y_1,xy)\delta(x-x_2)\delta(y-y_2)(1-\cos t)$$
$$-\Delta_{\mathrm{Ps}}(xy,x_2y_2)\delta(x-x_1)\delta(y-y_1)(1-\cos t)$$
$$+\Delta_{\mathrm{Ps}}(x_1y_1,xy)\Delta_{\mathrm{Ps}}(xy,x_2y_2)(1-\cos t)^2\ . \tag{B31}$$

As in the case of (B22), the correctness of this solution can be verified by direct substitution into (B29) [with (B20)], making use of (B23) and (B24).

Substituting the c functions into (B18), (B26), and (B28), putting $t=\pi/2$, and using (B1), (B2), and (1), one obtains the expression (21).

APPENDIX C: EVALUATION OF HYDROGEN TANI TRANSFORM

Defining

$$\hat{A}(t)=e^{-t\hat{F}_e}\hat{A}e^{t\hat{F}_e} \tag{C1}$$

in analogy with (B2), one has the equation of motion

$$\frac{d\hat{A}(t)}{dt}=[\hat{A}(t),\hat{F}_e]_-=[\hat{A}(t),\hat{F}_e(t)]_-\ , \tag{C2}$$

where by (16),

$$\hat{F}_e=\hat{F}_e(t)$$
$$=\sum_{\nu}[\hat{A}^\dagger_{\nu e}(t)\hat{e}_\nu(t)-\hat{e}^\dagger_\nu(t)\hat{A}_{\nu e}(t)]\ . \tag{C3}$$

The operators $\hat{e}_\nu$, $\hat{A}_{\nu e}$, and $\hat{e}(y)$ then satisfy the equations of motion

$$\frac{d\hat{e}_\nu(t)}{dt}=-\hat{A}_{\nu e}(t),\quad \frac{dA_{\nu e}(t)}{dt}=\hat{e}_\nu(t)\ ,$$
$$\frac{d\hat{e}(y,t)}{dt}=\sum_\nu\varphi_{\nu e}(y)\hat{e}_\nu(t)\ . \tag{C4}$$

The solution of the first two satisfying the initial conditions $\hat{A}(0)=\hat{A}$ is

$$\hat{e}_\nu(t)=\hat{e}_\nu\cos t-\hat{A}_{\nu e}\sin t\ ,$$
$$\hat{A}_{\nu e}(t)=\hat{e}_\nu\sin t+\hat{A}_{\nu e}\cos t\ . \tag{C5}$$

Substitution of this expression for $\hat{e}_\nu(t)$ into the third Eq. (C4) and integration from 0 to t yields (31) when $t=\pi/2$ [Eq. (16)].

APPENDIX D: POSITRONIUM BOUND-STATE KERNEL IN THE CENTER-OF-MASS SYSTEM

Upon inserting (13) into the definition (B23) of the positronium bound-state kernel and noting that summation over α stands for integration over the translational wave vector $\vec{k}$ and summation over the internal quantum numbers ν, one has

$$\begin{aligned}\Delta_{\mathrm{Ps}}(xy,x'y')&=(2\pi)^{-3}\sum_{\nu}\int d\vec{k}\,e^{i\vec{k}\cdot(\vec{r}_{\mathrm{c.m.}}-\vec{r}'_{\mathrm{c.m.}})}u_{\nu}(\vec{r}_{ep},\sigma_p,\sigma_e)u^{*}_{\nu}(\vec{r}'_{ep},\sigma'_p,\sigma'_e)\\&=\delta(\vec{r}_{\mathrm{c.m.}}-\vec{r}'_{\mathrm{c.m.}})\sum_{\nu}u_{\nu}(\vec{r}_{ep},\sigma_p,\sigma_e)u^{*}_{\nu}(\vec{r}'_{ep},\sigma'_p,\sigma'_e)\\&=\delta(\vec{r}_{\mathrm{c.m.}}-\vec{r}'_{\mathrm{c.m.}})\delta_{\sigma_p\sigma'_p}\delta_{\sigma_e\sigma'_e}\sum_{\nu}u_{\nu}(\vec{r}_{ep},\sigma_p,\sigma_e)u^{*}_{\nu}(\vec{r}'_{ep},\sigma_p,\sigma_e)\\&\equiv\delta(\vec{r}_{\mathrm{c.m.}}-\vec{r}'_{\mathrm{c.m.}})\delta_{\sigma_p\sigma'_p}\delta_{\sigma_e\sigma'_e}\Delta_{\mathrm{Ps}}(\vec{r}_{ep},\vec{r}'_{ep};\sigma_p,\sigma_e)\,.\end{aligned}\tag{D1}$$

Here $\vec{r}_{\mathrm{c.m.}}=\frac{1}{2}(\vec{r}_e+\vec{r}_p)$, $\vec{r}_{ep}=\vec{r}_e-\vec{r}_p$ and similarly for the primed variables. The Kronecker δ functions expressing the diagonality in the positron and electron spin variables arise because each u_ν is an eigenstate of the z components of both the positron and electron spins. Hence each u_ν is nonvanishing only for one value ($\uparrow$ or $\downarrow$) of σ_p and one value of σ_e, and

$$u_{\nu}(\vec{r}_{ep},\sigma_p,\sigma_e)u^{*}_{\nu}(\vec{r}'_{ep},\sigma'_p,\sigma'_e)$$

vanishes unless $\sigma_p=\sigma'_p$ and $\sigma_e=\sigma'_e$.

APPENDIX E: ASYMPTOTIC WAVE PACKETS AND CONSTRAINTS

Consider a wave packet of the asymptotic states $|\vec{k}\sigma_p,\nu)$ [Eq. (61)], defined by

$$\begin{aligned}|\chi\sigma_p,\nu)&=\int d\vec{k}\,\tilde{\chi}(\vec{k})\,|\,\vec{k}\sigma_p,\nu)\\&=\int d\vec{r}_p\chi(\vec{r}_p)\hat{p}^{\dagger}(\vec{r}_p\sigma_p)\hat{e}^{\dagger}_{\nu}|\,0\rangle\,,\end{aligned}\tag{E1}$$

where $\tilde{\chi}(\vec{k})$ is the wave function of the positron wave packet in $\vec{k}$ space and $\chi(\vec{r}_p)$ is the corresponding Schrödinger wave function

$$\chi(\vec{r}_p)=(2\pi)^{-3/2}\int\tilde{\chi}(\vec{k})e^{-i\vec{k}\cdot\vec{r}_p}d\vec{k}\,.\tag{E2}$$

Clearly

$$\hat{e}(y)\,|\,\chi\sigma_p,\nu)=0\tag{E3}$$

and hence, by (55), the first constraint (53) is satisfied,

$$\hat{N}'_a\,|\,\chi\sigma_p,\nu)=0\tag{E4}$$

and in addition one has by (59)

$$\begin{aligned}\hat{N}'_{\mathrm{Ps}}\,|\,\chi\sigma_p,\nu)=&\int dx'dy'd\vec{r}_p(x'y'\,|\,N'_{\mathrm{Ps}}\,|\,\vec{r}_p\sigma_p,\nu)\chi(\vec{r}_p)\hat{p}^{\dagger}(x')\hat{e}^{\dagger}(y')\,|\,0\rangle\\&+\sum_{\nu'}\int dx'd\vec{r}_p(x'\nu'\,|\,N'_{\mathrm{Ps}}\,|\,\vec{r}_p\sigma_p,\nu)\chi(\vec{r}_p)\hat{p}^{\dagger}(x')\hat{e}^{\dagger}_{\nu'}\,|\,0\rangle\,.\end{aligned}\tag{E5}$$

It then follows from the last two Eqs. (60) that the second constraint

$$\hat{N}'_{\mathrm{Ps}}\,|\,\chi\sigma_p,\nu)=0\tag{E6}$$

will be satisfied provided that

$$\int\Delta_{\mathrm{Ps}}(x'y';r_p\sigma_p,y)\chi(r_p)\varphi_{\nu e}(y)d\vec{r}_p dy=0\,.\tag{E7}$$

Here $\Delta_{\mathrm{Ps}}(x'y';r_p\sigma_p,y)$ is the positronium bound-state kernel $\Delta_{\mathrm{Ps}}(x'y',xy)$ with $x=(r_p\sigma_p)$. Inserting the decomposition (D1) of Δ_{Ps} in relative and center-of-mass coordinates, one sees that (E7) will be satisfied provided that

$$\int\Delta_{\mathrm{Ps}}(\vec{r}'_{ep},r_{ep};\sigma_p,\sigma_e)\chi(\vec{r}'_{\mathrm{c.m.}}-\tfrac{1}{2}\vec{r}_{ep})\varphi_{\nu e}(\vec{r}'_{\mathrm{c.m.}}+\tfrac{1}{2}r_{ep},\sigma_e)d\vec{r}_{ep}=0\tag{E8}$$

for each fixed value of $\vec{r}'_{ep}$ and $\vec{r}'_{\text{c.m.}}$ (and, of course, of ν, σ_p, and σ_e).

To complete the proof, we must show that (E8) is satisfied in the usual asymptotic limit of a wave packet χ localized infinitely far from the origin (i.e., from the H atom). The hydrogen orbital $\varphi_{\nu e}$ in (E8) is localized about the origin in the sense that it decreases exponentially as the distance $|\vec{r}'_{\text{c.m.}}+\frac{1}{2}\vec{r}_{ep}|$ becomes $\gg n a_0$, where a_0 is the Bohr radius and n the principal quantum number (included in the quantum number set ν). Furthermore, each positronium relative wave function $u^*_\nu(r_{ep},\sigma_p,\sigma_e)$ in (50) has a range of the same order of magnitude, $n' a_0$, as a function of $|\vec{r}_{ep}|$ [note from (E8) that the variables $\vec{r}_{ep}$ and $\vec{r}'_{ep}$ are to be interchanged in (50)]. The product $\Delta_{\text{Ps}}\varphi_{\nu e}$ in (E8) is therefore only appreciable when $|\vec{r}'_{\text{c.m.}}| \lesssim (n+\frac{1}{2}\bar{n})a_0$, where $\bar{n}$ is some mean principal quantum number for the positronium states contributing to the summation (50). Now choose the free positron wave packet χ in (E8) to be of the usual form used in justification of the S-matrix formulas of formal scattering theory, i.e.,

$$\chi(\vec{r})=f(\vec{r})e^{i\vec{k}\cdot\vec{r}}\,, \tag{E9}$$

where f is an envelope function localized about some point $\vec{r}_0$ and with range w. Then the integral (E8) will vanish exponentially as $r_0\to\infty$, and indeed already for $r_0 \gg w+(n+\bar{n})a_0$ with w fixed. Finally, let $w\to\infty$ so that χ approaches an unmodulated plane wave, and $|\chi\sigma_p,\nu)$ approaches the unperturbed asymptotic state $|\vec{k}\sigma_p,\nu)$. This is the limiting sense in which the constraints (53) are satisfied, justifying the use of (62) and hence application of standard methods of formal scattering theory without explicit consideration of the constraints. The argument is easily extended to the asymptotic final states $|\vec{k}_p\sigma_p,\vec{k}_e\sigma_e)$ for the reactive process $\text{Ps}+H\to e^+ + e^-$ by defining them by an appropriate asymptotic limit of wave-packet states

$$|\chi_p\sigma_p,\chi_e\sigma_e)=\int d^3\vec{r}_p d^3 r_e \chi_p(\vec{r}_p)\chi_e(r_e) \times\hat{p}^\dagger(r_p\sigma_p)\hat{e}^\dagger(r_e\sigma_e)|0\rangle\,, \tag{E10}$$

since it is easy to show that the constraints (53) are satisfied in the limit of infinite separation between the positron and electron wave packets χ_p and χ_e. Hence the reactive S-matrix elements (65) may also be evaluated without explicit consideration of the constraints.

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