Post-prior symmetrical first-order T matrix for charge transfer

Jack C. Straton
Department of Physics, Kansas State University, Manhattan, Kansas 66506

Marvin D. Girardeau
Department of Physics and Institutes of Theoretical Science and Chemical Physics, University of Oregon, Eugene, Oregon 97403

(Received 23 March 1989)

The Fock-Tani Hamiltonian is found for systems containing two protons and one electron. It is shown that a post-prior symmetrical T-matrix element for $a^+ + (b^+c^-) \rightarrow (a^+c^-) + b^+$ may be found from that of the simpler proton-proton-electron system if a and b are treated as isospin projections of a single type of nucleon. The Coulomb-exchange contribution to the inelastic (isospin flip) scattering of this system gives a first-order T-matrix that is completely symmetrical with respect to post and prior interactions and orthogonalizations, a symmetry of the exact T-matrix.

I. INTRODUCTION

Quantum-theoretic techniques have been shown[1,2] to be a powerful tool in calculations of atomic collision cross sections. The original formulation of Taylor and collaborators[1,2] was restricted primarily to processes describable conveniently in terms of single-particle operators, due to the use of only annihilation and creation operators for single electrons. The Fock-Tani representation was introduced as a generalized field-theoretic representation involving field operators and wave functions of bound composites as well as their unbound constituents. In the resulting representation[3–10] composites are treated exactly and obey elementary commutation relations, and unbound states are exactly orthogonal to bound states. Potentials between unbound states contain orthogonalizaton subtractions so that there is not enough energy to bind. Because of the subtractions, perturbation series are likely to be more convergent than conventional Born series. A calculation of charge exchange in proton-hydrogen collisions[9,10] produced a total cross section in agreement with experiment[11] for energies greater than 10 keV and differential cross sections in very good agreement with experiment[12] (at 25, 60, and 125 keV) for angles within 1 mrad of the forward direction.

Several formal results are also noteworthy. The first-order Fock-Tani rearrangement cross sections for proton-hydrogen collisions with and without the internuclear term agree to 10% (whereas the first Born results differ by 100%) thus fulfilling at first order Wick's observation[13] that the internuclear potential should give no contribution to the exact T-matrix. Also each term of the Fock-Tani Hamiltonian corresponds to a specific and immediately identifiable physical process. Because of the coupling of asymptotic states to only some terms in the Hamiltonian, due to the specific configuration of field operators, one can use the same unperturbed Hamiltonian for different initial and final asymptotic arrangement channels. As a consequence, in Fock-Tani representation the same potential appears in each of the alternate definitions of the exact T matrix[14]

$$T_{fi} = (\phi_f|\hat{V}|\Psi_i^+) = (\Psi_f^-|\hat{V}|\phi_i) \tag{1}$$

so that reactants, intermediate states, and products are treated symmetrically.

However, previous derivations[3–10] have contained the familiar post-prior discrepancy of reactive collision theory[15,16] through the form of the potentials and orthogonalizations in the matrix elements contained with $\hat{V}$ in (1). This is a result of the ordered-product form of the orthogonalization transformations to the initial and final bound states. Since the exact T matrix has no such discrepancy[17] it would be desirable to remove this discrepancy from the first-order T matrix.

In the present paper it is shown that a first-order T matrix that is completely post-prior symmetrical can be derived by introducing an isotopic spin notation for the variables, orthogonalizing to a single bound species, and then choosing a nucleon-hydrogen initial state and a corresponding final state with opposite isospin. The charge exchange T matrix is then given by the Coulomb-exchange term in the Fock-Tani potential. The present derivation also extends previous work to allow up to two dynamic protons and one electron (the I_{21} subspace[8] of the Hilbert space of pair-bound states), and also allows an additional charge fixed at the origin, which effectively extends the result to I_{31} or I_{22}. Since the derivation and description of the Fock-Tani representation have been presented in detail in the literature,[3–10,18] the present derivation will focus primarily on the alternatives to, and extensions of, previous approaches.

II. THE FOCK-TANI TRANSFORMATION

One starts with the Fock Hamiltonian (in coordinate representation),

$$\hat{H}_F = \int dX \hat{\psi}^\dagger(X)[T_p(X) + V_{\rm ex}(X)]\hat{\psi}(X) + \int d_x \hat{\psi}^\dagger(x)[T_e(x) + V_{\rm ex}(x)]\psi(x)$$
$$+ \int dX d_x \hat{\psi}^\dagger(X)\hat{\psi}^\dagger(x)[V_{p\text{-}e}(Xx) + W_{p\text{-}e}(Xx)]\hat{\psi}(x)\hat{\psi}(X)$$
$$+\tfrac{1}{2}\int dX dX' \hat{\psi}^\dagger(X)\hat{\psi}^\dagger(X')[V_{p\text{-}p}(XX') + W_{p\text{-}p}(XX')]\hat{\psi}(X')\hat{\psi}(X) \quad (2)$$

in which the T's are kinetic energy operators, the $V_{\rm ex}$'s are external potentials [which may arise if (2) is a center-of-mass (c.m.) Jacobi system or from placing the origin on the coordinates of a fourth particle[10,19]], the W's are inertial potentials arising from placing the origin on the coordinates of a fourth particle,[10,19] and $V_{\rm p\text{-}e}$, and $V_{\rm p\text{-}p}$ are two-body potentials. Integrations over $x = (\mathbf{r}_e, \sigma_e)$ include integration over the electron's spatial coordinates and a sum over fermionic spin. Integrations over $X = (\mathbf{r}_n, \sigma_n, \tau)$ include integration over the nucleon's spatial variables and sums over both fermionic and isotopic spin (if desired). If (2) represents an accelerated c.m. system obtained by putting the origin on a fourth particle[10,19] variables x and X contain the positions of the remaining physical particles, but if (2) represents a Jacobi c.m. system x and X contain the positions of "fictitious" particles relative to the center of mass. The masses in the T's are chosen accordingly. One can then define a Fermi annihilation operator for the nucleon (with isospin states A and B),

$$\hat{\psi}(X) = \begin{cases} \hat{\psi}_A(X_A)\,, & X = (X_A, A) \\ \hat{\psi}_B(X_B)\,, & X = (X_B, B) \end{cases} \quad (3)$$

that, with $\psi(x)$, the annihilation operator for the electron, satisfies the anticommutation relations

$$[\hat{\psi}(X), \hat{\psi}^\dagger(X')]_+ = \delta(X, X') \equiv \delta(X_\tau - X_{\tau'})\delta_{\tau\tau'}\,,$$
$$[\hat{\psi}(x), \hat{\psi}^\dagger(x')]_+ = \delta(x - x')\,,$$
$$[\hat{\psi}(X), \hat{\psi}^\dagger(x)]_+ = 0\,, \quad (4)$$
$$[\hat{\psi}(X), \hat{\psi}(X')]_+ = [\hat{\psi}(X), \hat{\psi}(x)]_+$$
$$= [\hat{\psi}(x), \hat{\psi}(x)']_+ = 0\,.$$

Introducing a generic bound-state index $\mu = (\alpha, s)$, where s takes on two values AC and BC, and generic bound-state wave functions

$$\phi_\mu(Xx) = \begin{cases} \phi_{\alpha,AC}(X_A x), & s = AC \text{ and } \tau = A \\ \phi_{\alpha,BC}(X_B x), & s = BC \text{ and } \tau = B \\ 0, & s = AC \text{ and } \tau = B \\ 0, & s = BC \text{ and } \tau = A \end{cases} \quad (5)$$

one can easily show that a generalized orthonormality relation

$$\int \phi^*_\mu(Xx)\phi_{\mu'}(Xx)dXdx = \delta_{\mu\mu'} = \delta_{\alpha\alpha'}\delta_{ss'} \quad (6)$$

holds (with s running over AC and BC) as a consequence of the orthonormality relations for the two conventional bound species $\phi_{\alpha,AC}(X_A x)$ and $\phi_{\alpha,BC}(X_B x)$. The corresponding generic composite creation operators $\hat{A}^\dagger_\mu$ are then

$$\hat{A}^\dagger_\mu = \int dX dx \phi_\mu(Xx)\hat{\psi}^\dagger(X)\hat{\psi}^\dagger(x), \quad (7)$$

which satisfy the commutation relation

$$[\hat{A}_\mu, \hat{A}^\dagger_{\mu'}]_- = \delta_{\mu\mu'} + \hat{C}_{\mu\mu'} \quad (8)$$

with

$$\hat{C}_{\mu\mu'} = -\int dX dX' K_{\mu\mu'}(X, X')\hat{\psi}^\dagger(X)\hat{\psi}(X')$$
$$-\int dx\, dx'\, K_{\mu\mu'}(x, x')\hat{\psi}^\dagger(x)\hat{\psi}(x')$$
$$\equiv \hat{C}^p_{\mu\mu'} + \hat{C}^e_{\mu\mu'}, \quad (9)$$
$$K_{\mu\mu'}(X, X') = \int \phi^*_\mu(X'x)\phi_{\mu'}(Xx)dx,$$

and

$$K_{\mu\mu'}(x, x') = \int \phi^*_\mu(Xx')\phi_{\mu'}(Xx)dX. \quad (10)$$

Of course the isospin indices may be ignored if they are not needed by setting $\tau \equiv A$.

The Fock Hamiltonian (2) and the states (7) are transformed using a unitary operator

$$\hat{U} = \exp\left(\frac{\pi}{2}\hat{F}\right) \quad (11)$$

where (anticipating the need for refinement) the lowest order term is

$$\hat{F}_{11} = \sum_\mu (\hat{A}^\dagger_\mu \hat{a}_\mu - \hat{a}^\dagger_\mu \hat{A}_\mu). \quad (12)$$

The $\hat{a}_\mu$ and $\hat{a}^\dagger_\mu$ operators are elementary Bose operators satisfying commutation relations

$$[\hat{a}_{\alpha s}, \hat{a}^\dagger_{\beta s'}]_\pm = \delta_{\alpha\beta}\delta_{ss'} \quad (13)$$

differing from (8) through the disappearance of the intractable operator term $\hat{C}_{\mu\mu'}$. The rotation

$$|\mu\rangle \;\rightarrow\; \hat{U}^{-1}|\mu\rangle \;\equiv\; |\mu) \quad (14)$$

redescribes the *composite* state $|\mu\rangle \equiv \hat{A}^\dagger_\mu|0\rangle$ as an *elementary-particle* state $|\mu)$. The compositeness of the

bound states is still present implicitly in the representation since the transformed Fock-Tani Hamiltonian $\hat{U}^{-1}\hat{H}_F\hat{U}$ is a functional of the bound-composite wave functions ϕ_μ since these enter into (11) via (7). However, all annihilation and creation operators, *including those* $\hat{a}_\mu$ *and* $\hat{a}_\mu^\dagger$ *representing the composites*, now satisfy elementary-particle commutation rules so that the standard field-theoretic techniques[20] (Wick's theorem, Green's functions, etc.) can be applied to composite-particle states. The transformation (11) acts on an enlarged state space I which is the graded direct product[5,8] of the standard Fock space and an "ideal-composite" space generated by the $\hat{a}_\mu^\dagger$ operators. The vacuum state of this enlarged space will be denoted by $|0)$. There is a subsidiary condition that ensures that the enlarged space is isomorphic with the original (physical) Fock space, which is discussed in the Appendix.

III. THE TRANSFORMATION ON I_{21}

Fock-Tani Hamiltonian on the I_{21} subspace is found by solving differential "equations of motion." For any operator O one can define

$$O(t) \equiv \hat{U}^{-1}O\hat{U} = e^{-tF}Oe^{tF} , \tag{15}$$

which leads to the differential equation

$$\frac{d}{dt}O(t) = e^{-tF}[O,F]e^{tF} \equiv [O(t),F] . \tag{16}$$

On the subspace I_{21}, including two protons and one electron,

$$\frac{d\hat{A}_\mu(t)}{dt} = \hat{a}_\mu(t) + \sum_\nu \hat{C}^p_{\mu\nu}(t)\,\hat{a}_\nu(t) + O[e^2] \tag{17}$$

and

$$\frac{d\hat{a}_\mu(t)}{dt} = -\hat{A}_\mu(t) , \tag{18}$$

where $O[e^2]$ refers to terms that annihilate two or more (free or bound) electrons. Subject to the initial condition $\hat{A}_\mu(0) = \hat{A}_\mu$, $\hat{a}_\mu(0) = \hat{a}_\mu$, the solution on the I_{11} subspace, on which the $\hat{C}^p_{\mu\nu}$ term gives no contribution, is easily seen to be

$$\hat{A}_\mu(t) = \hat{A}_\mu \cos t + \hat{a}_\mu \sin t \tag{19}$$

and

$$\hat{a}_\mu(t) = \hat{a}_\mu \cos t - \hat{A}_\mu \sin t , \tag{20}$$

which embodies the interpretation of $\hat{U}$ effecting a $\pi/2$ rotation on I_{11}. But a multiple-commutator solution[18] of (17) and (18), on I_{21}, yields secular terms, terms in addition to the trigonometric functions of t, that do not allow the rotational interpretation. The cause is seen to be that the generator, $\hat{F}_{11}$, contains only terms from the I_{11} subspace. To make (17) and (18) more symmetrical one could add a term depending on $\hat{C}^p_{\mu\nu}$ to either cancel the second term in (17) or add it to (18). Thus (12) will be extended to include

$$\hat{F}_{21} = \sum_{\mu,\nu}[\hat{A}^\dagger_\mu(\delta_{\mu\nu} + b\,\hat{C}^p_{\mu\nu})\hat{a}_\nu - \text{H.c.}] , \tag{21}$$

where H.c. stands for Hermitian conjugate. This gives the pair of equations,

$$\frac{d\hat{A}_\mu(t)}{dt} = \hat{a}_\mu(t) + \sum_\nu (1+b)\,\hat{C}^p_{\mu\nu}(t)\,\hat{a}_\nu(t) + b\sum_{\nu,\tau}\hat{C}^p_{\mu\nu}(t)\,\hat{C}^p_{\nu\tau}(t)\,\hat{a}_\tau(t) + O[e^2] \tag{22}$$

and

$$\frac{d\hat{a}_\mu(t)}{dt} = -A_\mu(t) - \sum_\nu b\,\hat{C}^p_{\mu\nu}(t)\,\hat{A}_\nu(t) . \tag{23}$$

Consider the operator

$$\hat{C}^p_{\mu\nu}(t) = -\int dX\,dX' K_{\mu\nu}(X,X')\hat{\psi}^\dagger(X,t)\hat{\psi}(X',t) . \tag{24}$$

At lowest order

$$\hat{\psi}^\dagger(X,t)\hat{\psi}(X',t) \simeq \hat{\psi}^\dagger(X)\hat{\psi}(X') . \tag{25}$$

By particle-number conservation, the next higher order term will involve products of

$$\hat{\psi}^\dagger(X_1)\hat{\psi}^\dagger(x_1)\psi(x_2)\psi(X_2) ,$$

$$\hat{a}^\dagger_\tau\psi\,(x_1)\,\psi(X_1) ,$$

or

$$\psi^\dagger(X_1)\psi^\dagger(x_1)\hat{a}_\tau . \tag{26}$$

Thus since $\hat{a}_\nu(t)$ and $\hat{A}_\nu(t)$ annihilate one electron and one proton each,

$$\begin{aligned} C^p_{\mu\nu}(t)\hat{a}_\nu(t) &= \hat{C}^p_{\mu\nu}\hat{a}_\nu(t) + O[p^3] + O[e^2] , \\ \hat{C}^p_{\mu\nu}(t)\hat{A}_\nu(t) &= \hat{C}^p_{\mu\nu}\hat{A}_\nu(t) + O[p^3] + O[e^2] , \end{aligned} \tag{27}$$

where $O[p^3]$ stands for terms that annihilate three or more protons.

A consistent solution that embodies the interpretation of $\hat{U}$ effecting a $\pi/2$ rotation on the Hilbert space I_{21} is found by setting $b = -\frac{1}{2}$,

$$\hat{A}_\mu(t) = \hat{A}_\mu \cos t + \sum_\nu(\delta_{\mu\nu} + \tfrac{1}{2}\,\hat{C}^p_{\mu\nu})\;\hat{a}_\nu \sin t + O[\phi^4] , \tag{28}$$

$$\hat{a}_\mu(t) = \hat{a}_\mu \cos t - \sum_\nu(\delta_{\mu\nu} - \tfrac{1}{2}\hat{C}^p_{\mu\nu})\hat{A}_\nu \sin t + O[\phi^4] , \tag{29}$$

where $O[\phi^4]$ stands for terms of fourth order in the bound state wave functions (5) that will not contract to lower order, using (6) or (8), in future operations. One must still solve the coupled equations for the Fermi operators

$$\frac{d\,\psi(x,t)}{dt} = \sum_{\mu,\nu}[\psi(x,t),\hat{A}_\mu^\dagger]\ (\delta_{\mu\nu} + b\,\hat{C}_{\mu\nu}^p)\hat{a}_\nu(t) = -\sum_{\mu,\nu}\int dX\phi_\mu(X,x)\psi^\dagger(X,t)(\delta_{\mu\nu} + b\,\hat{C}_{\mu\nu}^p)\,\hat{a}_\nu(t)\ , \tag{30}$$

$$\frac{d\,\psi(X,t)}{dt} = \sum_\mu \int dx\phi_\mu(Xx)\hat{\psi}^\dagger(x,t)\hat{a}_\mu(t)\ \ - \tfrac{1}{2}\sum_{\mu,\nu}\int dx\phi_\mu(Xx)\hat{\psi}^\dagger(x,t)\,\hat{C}_{\mu\nu}^p\,\hat{a}_\nu(t)$$

$$+\tfrac{1}{2}\sum_{\mu,\nu}\int dX' K_{\mu\nu}(X,X')[\hat{A}_\mu^\dagger(t)\hat{\psi}(X',t)\,\hat{a}_\nu(t) - \hat{a}_\mu^\dagger(t)\hat{\psi}(X',t)\,\hat{A}_\nu(t)]\ . \tag{31}$$

The solution for $\psi(x,t)$ on I_{21} is most easily generated by the multiple commutator technique.[18] Define, for any operator,

$$O(t) = e^{-tF}Oe^{tF} = \sum_{n=o}^{\infty}\frac{t^n}{n!}\,[O,F]_n\ ,$$

where

$$[O,F]_0 \equiv O$$

and

$$[O,F]_{n+1} \equiv [[O,F]_n,F]\ . \tag{32}$$

Then the first three nontrivial commutators of $\hat{\psi}(x)$ are

$$[\hat{\psi}(x),\hat{F}_{21}]_1 = \sum_{\mu,\nu}[\hat{\psi}(x),\hat{A}_\mu^\dagger](\delta_{\mu\nu} + b\hat{C}_{\mu\nu}^p)\,\hat{a}_\nu\ , \tag{30'}$$

$$[\hat{\psi}(x),\hat{F}_{21}]_2 = -\sum_{\mu,\nu}[\psi(x),A_\mu^\dagger]\ (\delta_{\mu\nu} + 2b\,\hat{C}_{\mu\nu}^p)\,\hat{A}_\nu, + O[p^3] + O[e^2] + O[\phi^5]\ , \tag{33}$$

and

$$[\hat{\psi}(x),F_{21}]_3 = -\sum_{\mu,\nu}[\hat{\psi}(x),\hat{A}_\mu^\dagger]\ [\delta_{\mu\nu} + (3b+1)\,\hat{C}_{\mu\nu}^p]\,\hat{a}_\nu + O[e^2] + O[p^3] + O[\phi^5]\ . \tag{34}$$

But since $b = -\frac{1}{2}$

$$[\hat{\psi}(x),\hat{F}_{21}]_3 = -[\hat{\psi}(x),\hat{F}_{21}]_1 + O(e^2) + O(p^3) + O(\phi^5)\ , \tag{35}$$

so that to this order

$$\hat{\psi}(x,t) = \hat{\psi}(x) + \sum_{\mu,\nu}[\hat{\psi}(x),\hat{A}_\mu^\dagger]\left[(\delta_{\mu\nu} - \tfrac{1}{2}\hat{C}_{\mu\nu}^p)\hat{a}_\nu\left(t - \frac{t^3}{3!} + \frac{t^5}{5!} - \cdots\right) - (\delta_{\mu\nu} - \hat{C}_{\mu\nu}^p)\hat{A}_\nu\left(1 - 1 + \frac{t^2}{2!} - \frac{t^4}{4!} + \cdots\right)\right]$$

$$= \psi(x) - \sum_{\mu,\nu}\int dX\ \phi_\mu(Xx)\psi^\dagger(X)[(\delta_{\mu\nu} - \tfrac{1}{2}\,\hat{C}_{\mu\nu}^p)\hat{a}_\nu\sin t - (\delta_{\mu\nu} - C_{\mu\nu}^p)\hat{A}_\nu(1-\cos t)]\ . \tag{36}$$

Note that $\hat{\psi}(x,0) = \psi(x)$.

The generator used previously[3-10,18] for the Fock-Tani transformation on I_{11} (in which b=0) would lead to secular terms, terms that are complicated power series in t rather than being trigonometric, which would not have allowed the interpretation of $\hat{U}$ as a $\pi/2$ rotation on the space of bound states. The same term added to F to give the simple solution for $\hat{A}_\mu(t)$ and $\hat{a}_\mu(t)$ and also gives a simple form for $\hat{\psi}(x,t)$.

The final step consists of substituting $\hat{A}_\mu(t)$, $\hat{a}_\mu(t)$, and $\psi(x,t)$, to third order in wave functions, into the differential equation (31) for $\hat{\psi}(X,t)$. Note that by the same argument that led to (27),

$$\psi(X',t)\hat{a}_\nu(t) = \psi(X')\hat{a}_\nu(t) + O[e^3] + O[p^2]\ , \tag{37}$$

$$\psi(X',t)\hat{A}_\nu(t) = \psi(X')\hat{A}_\nu(t) + O[e^3] + O[p^2]\ ,$$

so that

$$\frac{d\psi}{dt}(X,t) = \sum_{\mu} \int dx\ \phi_\mu(Xx)\ \hat{\psi}^\dagger(x) \left(\hat{a}_\mu \cos t - \hat{A}_\mu \sin t + \tfrac{1}{2} \sum_{\nu} \hat{C}^p_{\mu\nu} \hat{A}_\nu \sin t - \tfrac{1}{2} \sum_{\nu} \hat{C}^p_{\mu\nu} (\hat{a}_\nu \cos t - \hat{A}_\nu \sin t) \right)$$
$$- \sum_{\mu\nu} \int dX' K_{\mu\nu}(XX') \Big(\{ \hat{a}^\dagger_\mu \hat{\psi}(X')\ (\hat{a}_\nu \sin t\ \cos t - \hat{A}_\nu \sin^2 t)$$
$$- \hat{A}^\dagger_\mu \hat{\psi}(X') [\hat{a}_\nu (\cos t - \cos^2 t)\ - \hat{A}_\nu (\sin t - \sin t\ \cos t)] \}$$
$$- \tfrac{1}{2} \sum_{\gamma} \hat{a}^\dagger_\mu \psi(X')\ \hat{C}^p_{\gamma\nu}\ \hat{a}_\nu\ \sin t\ \cos t - \tfrac{1}{2} \hat{a}^\dagger_\mu \hat{\psi}(X') (\hat{a}_\nu \sin t\ \cos t - \hat{A}_\nu \sin^2 t)$$
$$- \tfrac{1}{2} \hat{A}^\dagger_\mu \psi(X') (\hat{a}_\nu \cos^2 t - \hat{A}_\nu \sin t\ \cos t)$$
$$+ \tfrac{1}{2}\ \hat{a}^\dagger_\mu \psi(X') (\hat{a}_\nu\ \sin t\ \cos t + \hat{A}_\nu \cos^2 t) + \tfrac{1}{2} \sum_{\gamma} \hat{C}^p_{\nu\gamma}\ \hat{a}_\gamma\ \sin t\ \cos t$$
$$- \tfrac{1}{2} \hat{A}^\dagger_\mu \psi(X')\ (\hat{A}_\nu \sin t\ \cos t + \hat{a}_\nu \sin^2 t) \Big) + O[\phi^5] + O[p^2] \,. \tag{38}$$

Integration gives the final result on I_{21}

$$\psi(X,t) = \psi(X) + \sum_{\mu} \int dx \phi_\mu(Xx)\ \hat{\psi}^\dagger(x) [\hat{a}_\mu \sin t - \hat{A}_\mu (1 - \cos t)]$$
$$- \sum_{\mu,\nu} \int dx\ \phi_\mu(Xx)\ \hat{\psi}^\dagger(x) \hat{C}^p_{\mu\nu}\ [\tfrac{1}{2} \hat{a}_\nu \sin t - A_\nu (1 - \cos t)] - \sum_{\mu,\nu} \int dX' K_{\mu\nu}(X,X') \hat{A}_{\mu\nu}(t) \hat{\psi}(X')$$
$$- \tfrac{1}{8} \sum_{\mu,\nu} \int dx dX' dx' dY \phi^*_\mu(Yx)\ \Delta(Xx, X'x')\ \phi_\nu(Yx')\ \hat{a}^\dagger_\mu\ \hat{\psi}(X')\ \hat{a}_\nu \sin^2 t \,, \tag{39}$$

where

$$\hat{A}_{\mu\nu}(t) = \tfrac{1}{2}\ \hat{a}^\dagger_\mu\ \hat{a}_\nu \sin^2 t + \hat{a}^\dagger_\mu\ \hat{A}_\nu (\tfrac{1}{2}\ \sin t\ \cos t - \tfrac{1}{2} t + \tfrac{1}{2} t)$$
$$- \hat{A}^\dagger_\mu\ \hat{a}_\nu (\sin t - \tfrac{1}{2} \sin t\ \cos t - \tfrac{1}{2} t + \tfrac{1}{2} t)$$
$$+ \hat{A}^\dagger_\mu\ \hat{A}_\nu (1 - \cos t - \tfrac{1}{2} \sin^2 t) \,. \tag{40}$$

Note that the cancellation in the secular terms, linear in t, is again a result of the new term in the generator (21). In the Appendix it is shown that this new term in the generator also allows the subsidiary condition to be satisfied to third order in wave functions even in media of nonzero density.

One may show by substitution into the differential equations (17), (18), (30), and (31) that (28), (29), (36), and (39) are a self-consistent set of solutions to fourth order in wave functions on I_{21}. Finally, the transformed operators are found by setting $t = \pi/2$.

IV. THE FOCK-TANI HAMILTONIAN

It is now a straightforward matter to evaluate the Fock-Tani Hamiltonian by substituting (36) and (39) into (2) and applying Wick's theorem to rearrange all terms into normal order. Since this algebraic reduction parallels that previously carried out,[4] only the final results, up through binary collision terms, will be given here. As previously, $H_{\rm FT}$ has the general structure

$$\hat{H}_{\rm FT} = \hat{H}_p + \hat{H}_e + \hat{V}_{\rm pp} + \hat{H}_{\rm pe} + \hat{H}_a + \hat{H}_{\rm ap}$$
$$+ \hat{H}(pe \leftarrow a) + \hat{H}(a \leftarrow pe)$$
$$+ \hat{H}(ppe \leftarrow pa) + \hat{H}(pa \leftarrow ppe) + \cdots \,, \tag{41}$$

where the subscripts refer to the occupation number of the three species. As previously, the terms $\hat{H}_p$, $\hat{H}_e$, and $\hat{V}_{\rm pp}$ are the same as the corresponding terms (single-proton, single-electron, and p-p interaction possibly in the presence of a charge fixed at the origin) in the standard Fock Hamiltonian

$$\hat{H}_p = \int dX\ \hat{\psi}^\dagger(X)\ T(X) \hat{\psi}(X) \,,$$
$$\hat{H}_e = \int dx\ \hat{\psi}^\dagger(x) T(x) \hat{\psi}(x) \,, \tag{42}$$
$$V_{pp} = \tfrac{1}{2} \int dX dX'\ \hat{\psi}^\dagger(X) \hat{\psi}^\dagger(X')\ \ V(XX') \hat{\psi}(X^\dagger) \hat{\psi}(X) \,,$$

where the possible presence of a charge fixed at the origin is included by defining

$$T(X) = T_p(X) + V_{\rm ex}(X) \,,$$
$$T(x) = T_e(x) + V_{\rm ex}(x) \,,$$
$$V(X,X') = V_{p\text{-}p}(X,X') + W_{p\text{-}p}(X,X') \,, \tag{43}$$
$$V(X,x) = V_{p\text{-}e}(X,x) + W_{p\text{-}e}(X,x) \,.$$

The physical interpretation of these terms in $\hat{H}_{\mathrm{FT}}$ is, however, quite different from their interpretation in $\hat{H}_F$, in that the $\hat{\psi}$ and $\hat{\psi}^\dagger$ operators now refer only to *unbound* (i.e., ionized) protons and electrons. All bound state contributions are contained in other terms in $\hat{H}_{\mathrm{FT}}$ involving the atomic annihilation and creation operators $\hat{a}_\mu$ and $\hat{a}_\mu^\dagger$. Atomic binding has an indirect effect on the proton-electron interaction term in $\hat{H}_{pe}$, which differs from the bare proton-electron interaction from $V(X,X')$ in H_F. As previously,[4] $\hat{H}_{pe}$ is found to be a nonlocal interaction operator

$$\hat{H}_{pe} = \int dX\,dx\,dX'\,dx'\hat{\psi}^\dagger(X)\hat{\psi}^\dagger(x) \times(Xx|H|X'x')\hat{\psi}(x')\hat{\psi}(X') \tag{44}$$

with matrix element

$$\begin{aligned}(Xx|H|X'x') = {} & V(Xx)\delta(X-X')\delta(x-x') \\ & -H(Xx)\Delta(Xx,X'x') \\ & -[H(X'x')\Delta(X'x',Xx)]^* \\ & +\int \Delta(Xx,Yy)H(Yy)\Delta(Yy,X'x') \\ & \times dY\,dy\ . \end{aligned} \tag{45}$$

Here Δ is the bound-state kernel

$$\Delta(Xx,X'x') = \sum_\alpha \phi_\alpha(Xx)\phi_\alpha^*(X'x') \tag{46}$$

(which has been shown previously[8] to be diagonal in spin indices), the kernel of the projection operator onto the *bound*-atom subspace, and $H(Xx)$ is the single-atom Schrödinger Hamiltonian

$$H(Xx) = T(X) + T(x) + V(Xx)\ . \tag{47}$$

Introduce the standard decomposition of the ϕ's appearing in (5)

$$\phi_{\alpha,s}(X_\tau x) = \Omega^{-1/2}\, e^{i\mathbf{k}\cdot\mathbf{R}_\tau}\, u_\nu(\mathbf{r}-\mathbf{R}_\tau,\sigma_p,\sigma_e)\ , \tag{48}$$

where $\alpha = (\mathbf{k},\nu)$ with $\mathbf{k}$ the translational wave vector, ν all other quantum numbers, Ω the volume element of the system (periodic boundary conditions may be chosen for convenience), and u_ν the atomic wave functions in the c.m. system. Then one can easily show[2] that Δ has a range $\sim (m/M)a_o$ with respect to the nuclear separation $\mathbf{R}_A - \mathbf{R}_B$ and range $\sim a_o$ with respect to the electron-nucleus separations $\mathbf{r}-\mathbf{R}_A$ and $\mathbf{r}-\mathbf{R}_B$, where m is the electron mass, M the proton mass, and a_o the Bohr radius. It follows that the matrix element (45) consists of a local "bare Coulomb interaction" term (the first V term) and a nonlocal interaction of the opposite sign and range $\sim a_o$, which partially cancels the attractive p-e Coulomb interaction. This cancellation is more evident in the special case in which the $\phi_{\alpha,s}$ are chosen to be free-atom energy eigenstates satisfying

$$\begin{aligned} H(Xx)\phi_{\alpha,s}(Xx) &\equiv [T(X)+T(x)+V(Xx)]\phi_{\alpha,s}(Xx) \\ &= \varepsilon_\alpha\phi_{\alpha,s}(Xx)\ . \end{aligned} \tag{49}$$

Then (45) simplifies to

$$\begin{aligned}(Xx|H|X'x') = {} & V(Xx)\delta(X-X')\delta(x-x') \\ & -\sum_\alpha \varepsilon_\alpha\phi_\alpha(Xx)\phi_\alpha^*(X'x')\ . \end{aligned} \tag{50}$$

This cancellation weakens the p-e attraction so much that (44) no longer supports bound states, as has been shown previously.[21] This is important since the bound-state effects are already contained in other terms involving the $\hat{a}_\mu$ and $\hat{a}_\mu^\dagger$. The situation here is very similar to that obtaining in Weinberg's "quasiparticle method"[22] for scattering from a potential with bound states. He found that the weakened interaction kernel led to greatly improved convergence of the Born series for scattering. One expects a similar benefit here, although our system is much more complicated (many body instead of single particle).

Of the other terms in (41), the single atom Hamiltonian $\hat{H}_a$ has the previously found form[14]

$$\hat{H}_a = \sum_{\alpha,\beta}\hat{a}_\alpha^\dagger(\alpha|H|\beta)\hat{a}_\beta \tag{51}$$

with

$$(\alpha|H|\beta) = \int \phi_\alpha^*(Xx)H(Xx)\phi_\beta(Xx)dX\,dx\ , \tag{52}$$

reducing to

$$\hat{H}_a = \sum_\alpha \varepsilon_\alpha\hat{a}_\alpha^\dagger\,\hat{a}_\alpha + \sum_{\alpha,\beta}\int \phi_\alpha^*(Xx)\,\hat{a}_\alpha^\dagger[V_{\mathrm{ex}}(X)+V_{\mathrm{ex}}(x)] \times\hat{a}_\beta\,\phi_\beta(Xx)dX\,dx \tag{53}$$

in the case (49). Similarly, the ionization and recombination terms are

$$\hat{H}(pe\leftarrow a) = \sum_\alpha\int dX\,dx\ \hat{\psi}^\dagger(X)\ \hat{\psi}^\dagger(x)(Xx|H|\alpha)\hat{a}_\alpha\ , \tag{54}$$

$$\hat{H}(a\leftarrow pe) = [\hat{H}(pe\leftarrow a)]^\dagger\ ,$$

with

$$\begin{aligned}(Xx|H|\alpha) = {} & H(Xx)\phi_\alpha(Xx) \\ & -\int\Delta(Xx,Yy)H(Yy)\phi_\alpha(Yy)dY\,dy\ , \end{aligned} \tag{55}$$

which vanishes in the case (49) of stationary (hence nondecaying) energy eigenstates with no external potentials, or reduces to

$$(Xx|H|\alpha) = [V_{\mathrm{ex}}(X)+V_{\mathrm{ex}}(x)]\,\phi_\alpha(Xx) - \int\Delta(Xx,Yy)\,[V_{\mathrm{ex}}(Y)+V_{\mathrm{ex}}(y)]\,\phi_\alpha(Yy)dY\,dy \tag{56}$$

if the atom is in the presence of nonzero external potentials. The term

$$\hat{H}_{ap} = \sum_{\alpha,\beta} \int dX dX' \, \hat{a}^\dagger_\alpha \, \hat{\psi}^\dagger(X)(\alpha X|H|\beta X') \, \hat{\psi}(X') \, \hat{a}_\beta \tag{57}$$

has a matrix element that is a sum of local direct Coulomb interactions

$$(\alpha X|H|\beta X')_{\text{Coul}} = \delta(X - X') \int \phi^*_\alpha(Yy)[V(XY) + V(Xy)] \, \phi_\beta(Yy) dY dy \, , \tag{58}$$

nonlocal orthogonalization corrections to the direct interaction,

$$\begin{aligned}(\alpha X|H|\beta X')_{\text{orthog}} = -\int \phi^*_\alpha(Yx)[\tfrac{3}{4}T(Y) + \tfrac{1}{2}T(x) + \tfrac{1}{2}T(x') + \tfrac{1}{8}T(X) + \tfrac{1}{8}T(X') \\ + \tfrac{1}{2}V(Yx) + \tfrac{1}{2}V(Yx') + \tfrac{1}{2}V(YX) + \tfrac{1}{2}V(YX') + \tfrac{1}{2}V(Xx) \\ + \tfrac{1}{2}V(X'x')]\Delta(Xx, X'x')\phi_\beta(Yx')dx dx' dY \, ,\end{aligned} \tag{59}$$

Coulomb-exchange coupling matrix elements including an orthogonalization correction (the terms involving Δ),

$$\begin{aligned}(\alpha X|H|\beta X')_{\text{Coul-ex}} = &-\int \phi^*_\alpha(X'x)\{V(XX') + \tfrac{1}{2}[V(Xx) + V(X'x)]\}\phi_\beta(Xx)dx \\ &+\tfrac{1}{2}\int \phi^*_\alpha(Yx)[V(YX) + V(Xx)]\Delta(Yx, X'x')\phi_\beta(Xx')dx dx' dY \\ &+\tfrac{1}{2}\int \phi^*_\alpha(X'x)\Delta(Xx, Yx')[V(YX') + V(X'x')\phi_\beta(Yx')dx dx' dY \, ,\end{aligned} \tag{60}$$

and intra-atomic-energy–exchange coupling matrix elements including an orthogonalization correction,

$$\begin{aligned}(\alpha X|H|\beta X')_{\text{intra-ex}} = &-\tfrac{1}{2}\int \{\phi^*_\alpha(X'x)H(Xx)\phi_\beta(Xx) + [H(X'x)\phi_\alpha(X'x)]^*\phi_\beta(Xx)\}dx \\ &+\tfrac{1}{2}\int \phi^*_\alpha(Yx)H(Yx)\Delta(Yx, X'x')\phi_\beta(Xx')dx dx' dY \\ &+\tfrac{1}{2}\int \phi^*_\alpha(X'x)\Delta(Xx, Yx')H(Yx')\phi_\beta(Yx')dx dx' dY \, .\end{aligned} \tag{61}$$

In the case (49), ϕ_α free-atom energy eigenstates with no external potentials, the matrix element (61) can be shown to vanish by an argument analogous to that demonstrating the vanishing of (55) in the same case. Such cancellations show that the fourth-order (in wave functions) orthogonalization corrections can be very important. If external potentials are present (61) reduces to

$$\begin{aligned}(\alpha X|H|\beta X')_{\text{intra-ex}} = &-\int \phi^*_\alpha(X'x)\{\tfrac{1}{2}[V_{\text{ex}}(X) + V_{\text{ex}}(X')] + V_{\text{ex}}(x)\}\phi_\beta(Xx)dx \\ &+\tfrac{1}{2}\int \phi^*_\alpha(Yx)[V_{\text{ex}}(Y) + V_{\text{ex}}(x)]\Delta(Yx, X'x')\phi_\beta(Xx')dx dx' dY \\ &+\tfrac{1}{2}\int \phi^*_\alpha(X'x)\Delta(Xx, Yx')[V_{\text{ex}}(Y) + V_{\text{ex}}(x')]\phi_\beta(Yx')dx dx' dY \, .\end{aligned} \tag{61'}$$

Consider next the term representing atomic ionization due to a proton-atom collision, and the inverse recombination term,

$$\begin{aligned}&\hat{H}(ppe \leftarrow pa) = \sum_\alpha \int dX dx dX' dX'' \, \hat{\psi}^\dagger(X)\psi^\dagger(x)\hat{\psi}^\dagger(X') \, (XxX'|H|\alpha X'')\hat{\psi}(X'')\hat{a}_\alpha \, , \\ &\hat{H}(pa \leftarrow ppe) = [\hat{H}(ppe \leftarrow pa)]^\dagger \, ,\end{aligned} \tag{62}$$

with matrix element

$$\begin{aligned}(XxX'|H|\alpha X'') = &\, \delta(X' - X'')[V(XX') + V(X'x)]\phi_\alpha(Xx) \\ &-\delta(X' - X'')\int \Delta(Xx, Yy)[V(X'Y) + V(X'y)]\phi_\alpha(Yy)dY dy \\ &+\int [\Delta(Xx, X''y)H(X'y) + \tfrac{1}{2}H(Xx)\Delta(Xx, X''y)]\phi_\alpha(X'y)dy \\ &+\int \Delta(Xx, X''y)[\tfrac{1}{2}V(X'x) + V(X'X'') + \tfrac{1}{2}V(XX') + V(X''y)]\phi_\alpha(X'y)dy \, .\end{aligned} \tag{63}$$

This is similar to, but not identical with, the previous expression;[4] in particular, the secular terms (proportional to π) occuring previously are now absent, as expected physically.

This completes the evaluation of the single-species Fock-Tani Hamiltonian through fourth-order in bound-state wave function on the subspace including up to two protons and one electron, I_{21}, and possibly a fourth particle fixed at the origin that effectively allows calculations on I_{22} or I_{31}. For further details regarding physical interpretations and diagrammatic representations of the various terms in (41), the original work[4] should be consulted. The operator structure of all the terms are the same here as previously, but some of the matrix elements are changed, particularly with regard to cancellation of all secular terms and the inclusion of some fourth-order orthogonalization terms previously omitted. If the isotopic spin formalism included in this Hamiltonian is not needed one can ignore it by setting $\tau \equiv A$ in the definitions of Sec. III.

V. THE SYMMETRICAL FIRST-ORDER T MATRIX FOR REACTIVE COLLISIONS ON I_{21}

Consider a system containing three types of constituents denoted by A, B, and C, and suppose that these can form both (BC) and (AC) bound states, but not (AB) or (ABC). The isospin notation of the previous sections, in which fermionic constituents of type A and B are regarded as the same kind of particle in different internal states (as protons and neutrons are regarded as different states of the nucleon), has the (very great) advantage that the Fock-Tani Hamiltonian for the two-species case, relevant to reactions

$$A + (BC) \rightarrow (AC) + B \ , \tag{64}$$

is already present in the one-species Hamiltonian (41). This treatment is more symmetrical than the two-species Hamiltonian previously derived from an ordered product transformation[5] (unsymmetrical with respect to the various species).

Also, on the one-A, one-B, one-C subspace, the assumption that all three constituents are fermions is actually only a convenience, allowing immediate adaptation of the results of the previous sections. Exchange effects cannot occur on this subspace, so the reaction cross section is independent of the choice of statistics of the three constituents. Although the sign of the amplitudes depends on the choice, the signs cancel from the cross section. The results are then immediately applicable to a reaction like $D^+ + H \rightarrow D + H^+$ in which D^+ is a boson and H^+ a fermion, and in general to (64) for any choice of A, B, and C (assuming, however that A, B, and C are distinct species).

The Fock-Tani Hamiltonian for (64) has recently been derived by Ficocelli Varracchio[18] and Ojha *et al.*[9] using the multispecies Fock-Tani transformation of Girardeau and Gilbert[5] in ordered product form $\hat{U}_{BC}\hat{U}_{AC}$. The first-order matrix elements exhibit a post-prior discrepancy related to the arbitrariness of this ordering, the opposite order $\hat{U}_{AC}\hat{U}_{BC}$ being also allowed (since A, B, and C are distinguishable) but giving different matrix elements. On the contrary, the matrix element that will be obtained herein is symmetrical with respect to the (BC) and (AC) composites and therefore treats the post and prior interactions on an equal footing.

The first-order approximation ("Fock-Tani first Born") to the T matrix for (64) can be obtained from the proton-hydrogen scattering matrix element $(\alpha X|H|\beta X')$, (57) through (61), by the substitutions

$$X' = (X_A, A), \ X = (X_B, B) \ ,$$
$$\beta \rightarrow \mu_i = (\alpha_i, BC), \ \alpha \rightarrow \mu_f = (\alpha_f, AC) \ , \tag{65}$$

in accordance with the previously described generalized isotopic spin notation of Sec. II. Note that X_A is the coordinate of the incoming A particle and X_B that of the outgoing B particle. The transition amplitude for given initial and final momenta k_A and k_B of the A particle and B particle can then be obtained by Fourier transformation with respect to X_A and X_B. The direct Coulomb contribution $(\alpha X|H|\beta X')_{\text{Coul}}$ of (58) vanishes in the present case because $\delta(X - X')$ contains the factor $\delta_{BA} = 0$, B and A being distinct species. Similarly, the orthogonalization contribution $(\alpha X|H|\beta X')_{\text{orthog}}$ (59) vanishes identically in X_A, X_B, X_C, and X'_C whenever $X = (X_B, B)$ and $X'(X_A, A)$, as a consequence of (5). Furthermore, taking the $\phi_{\alpha,AC}$ and $\phi_{\alpha,BC}$ to be energy eigenstates of the (AC) and (BC) systems will cause the expression $(\alpha X|H|\beta X')_{\text{intra-ex}}$ (61) to vanish, as previously noted. Therefore, only the expression $(\alpha X|H|\beta X')_{\text{Coul-ex}}$ (60) is needed to determine the desired reaction amplitude.

With the aforementioned substitutions and in an obvious notation, (60) becomes

$$\begin{aligned}
(\mu_f X|H|\mu_i X')_{\text{Coul-ex}} &= (\alpha_f, AC; X_B, B|H|\alpha_i, BC; X_A, A) \\
&= -\int \phi^*_{\alpha_f,AC}(X_A, A; x_C)\{V(X_A X_B) + \tfrac{1}{2}[V(X_B x_C) + V(X_A x_C)]\}\phi_{\alpha_f,BC}(X_B, B; x_C)dx_C \\
&\quad + \tfrac{1}{2}\int \phi^*_{\alpha_f,AC}(Y x_C)[V(Y; X_B, B) + V(X_B x_C)]\ \Delta(Y x_C|X_A, A; x'_C) \\
&\qquad \times \phi_{\alpha_i,BC}(X_B, B; x'_C)dx_c dx'_c dY \\
&\quad + \tfrac{1}{2}\int \phi^*_{\alpha_f,AC}(X_A, A; x_C)\ \Delta(X_B, B; x_C|Y x'_C)[V(Y; X_A, A) \\
&\qquad + V(X_A x'_C)]\phi_{\alpha_i,BC}(Y x'_C)dx_c dx'_c dY \ .
\end{aligned} \tag{66}$$

In the orthogonalization integrals (the ones involving Δ), Y stands for (Y,τ) and $\int dY$ for $\sum_\tau \int dY$, with τ running over A and B. By (5) only $\tau = A$ contributes to the first orthogonalization integral and $\tau = B$ to the second. Then reverting to standard notation and denoting the amplitude (66) simply by $(\alpha_f X_B|V|\alpha_i X_A)$, one finds

$$(\alpha_f X_B|V|\alpha_i X_A) = -\int \phi^*_{\alpha_f,AC}(X_A x_C)\{V(X_A X_B)+\tfrac{1}{2}[V(X_B x_C)+V(X_A x_C)]\}\phi_{\alpha_i,BC}(X_B x_C)dx_C$$
$$+\tfrac{1}{2}\int \phi^*_{\alpha_f,AC}(X'_A x'_C)[V(X'_A X_B)+V(X_B x'_C)]\,\Delta_{AC}(X'_A x'_C, X_A x)\phi_{\alpha_i,BC}(X_B x_C)dX'_A dx'_C dx_C$$
$$+\tfrac{1}{2}\int \phi^*_{\alpha_f,AC}(X_A x_C)\,\Delta_{BC}(X_B x_C, X'_B x'_C)[V(X_A X'_B)+V(X_A x'_C)]\phi_{\alpha_i,BC}(X'_B x'_C)dX'_B dx'_C dx_C\ . \tag{67}$$

This is only a first approximation (Fock-Tani first Born) to the exact T matrix element for (64), but it goes well beyond a conventional first Born approximation. Higher-order corrections involve other terms in the Fock-Tani Hamiltonian [i.e., terms other than (57)], which contribute through virtual intermediate states in higher-order terms in the Fock-Tani Born series. These other terms in $\hat{H}_F$ can also be determined from the corresponding terms in (41) by the same generalized isotopic spin technique, but will not be exhibited here.

It is of interest to compare (67) with the expressions of Ficocelli Varracchio[18] and Ojha *et al.*[9] based on the ordered-product[5] form of the Fock-Tani transformation. Assuming the $\phi_{\alpha,AC}$ and $\phi_{\beta,BC}$ to be energy eigenstates of the isolated (AB) and (BC) systems as before, the expression of Ojha *et al.*[9] is, in the present notation,

$$(\alpha_f X_B|V|\alpha_f X_A)_{GG} = \int \phi^*_{\alpha_f,AC}(X_A x_C)[V(X_A X_B)+V(X_A x_c)]\phi_{\alpha_i,BC}(X_B x_C)dx_C$$
$$-\int \phi^*_{\alpha_f,AC}(X_A x_C)\Delta_{BC}(X_B x_C, X'_B x'_C)[V(X_A X'_B)+V(X_A x'_C)]\phi_{\alpha_i,BC}(X'_B x'_C)dX'_B dx'_C dx_C \tag{68}$$

where the subscript GG is a reminder that this expression derives from the Girardeau-Gilbert ordered-product form[5] of the Fock-Tani transformation. The derivation of Ficocelli Varracchio[18] proceeded from the same starting point[5] but was for the more general case of a three-body potential (for example, a Born-Oppenheimer potential between the three nuclei involved in an atom-diatom reaction) that can be specialized to the present problem by expressing it as a sum of pair potentials,

$$V(X_A X_B x_C) = V(X_A X_B)+V(X_A x_C)+V(X_B x_C)\ . \tag{69}$$

Then if $\phi_{\alpha,AC}$ and $\phi_{\beta,BC}$ are again chosen to be energy eigenstates, his expression [his Eq.(68)] reduces, in the present notation, to precisely the same formula (68). As has been noted previously,[9,18] this expression exhibits the familiar "post-prior" discrepancy of reactive collision theory, in that initial- and final-state interactions and orthogonalizations are not treated on an equal footing. $V(X_A X_B)$ and $V(X_A x_C)$ are the interactions of the incoming A particle with the particles of the incoming (BC) bound state, and subtraction terms involving Δ_{BC} orthogonalize $(V_{AB}+V_{AC})\phi_{\alpha_i,BC}$ to the manifold of all (BC) bound states. In other words, this matrix element represents the *prior* form of the first Born matrix element, corrected by *prior* orthogonalization. This stems from the unsymmetrical form $\hat{V}_{BC}\hat{V}_{AC}$ of the transformation. In a case such as this where A, B, and C species are all distinct, the alternative form $\hat{V}_{AC}\hat{V}_{BC}$ is also allowed,[5] but leads to an equally unsymmetrical matrix element

$$(\alpha_f X_B|V|\alpha_i X_A)_{post} = \int \phi^*_{\alpha_f,AC}(X_A x_C)[V(X_A X_B)+V(X_B x_C)]\phi_{\alpha_i,BC}(X_B x_C)dx_C$$
$$-\int \phi^*_{\alpha_f,AC}(X'_A x'_C)[V(X'_A X_B)+V(X_B x'_C)]\Delta_{AC}(X'_A x'_C, X_A x_C)\phi_{\alpha_i,BC}(X_B x_C)dX'_A dx'_C dx_C\ , \tag{70}$$

involving only *post* interactions $V(X_A X_B)$ and $V(X_B x_C)$ and a *post* orthogonalization involving the kernel Δ_{AC}. *Exact* T-matrix elements involve no such discrepancy, as is well known.[17] It is, therefore, noteworthy that the improved first-order matrix element (67) is completely symmetrical with respect to post and prior interactions and orthogonalizations. In fact, it can be written as an average of post and prior matrix elements,

$$(\alpha_f X_B|V|\alpha_i X_A) = -\tfrac{1}{2}[\,(\alpha_f X_B|V|\alpha_i X_A)_{post} + (\alpha_f X_B|V|\alpha_i X_A)_{prior}]\ , \tag{71}$$

where $(\alpha_f X_B|V|\alpha_i X_A)_{prior}$ is $(\alpha_f X_B|V|\alpha_i X_A)_{GG}$ of (68). The minus sign in (71) has no physical significance,

being merely a result of the phase choice, which disappears when the matrix element is squared in forming the cross section.

VI. CONCLUSION

The original motivation for this paper was the extension of the Fock-Tani transformation to systems containing two protons and one electron, with the possibility of a fourth charge fixed at the origin. This is the initial, and most difficult, of the three transformations necessary to calculate the Fock-Tani T matrix for reactions of the type $A+(BCD) \rightarrow (AB)+(CD)$, where (BCD) could be an atom such as helium or hydrogen-minus.

The representation developed here has three benefits not originally contemplated; the elimination of secular terms appearing in previous[4] treatments, the satisfaction of the subsidiary condition to third order (in wave functions) for states of nonzero density (see the Appendix), and a first-order T matrix for reactive collisions that has the post-prior symmetry of the exact T matrix. The ordered product form[5] of the Fock-Tani transformation added a post-prior asymmetry to the first Born approximation, which is post-prior symmetrical for a collision of a structureless particle on a hydrogenic target. This consequence is typical of other first-order theories that seek to improve upon the results of the Born approximation, such as the distorted-wave Born approximation (DWBA) of Shakeshaft and Wadehra[23] and the Eikonal approximation.[24] For the special case $M_C << M_A, M_B$ this DWBA regains post-prior symmetry for capture into the ground state but not for capture into excited states. Burgdorfer and Taulbjerg have developed a DWBA (Ref. 25) that retains post-prior symmetry on the energy shell. The present Fock-Tani T matrix, however, remains post-prior symmetrical without either of these restrictions. Whether a similar formalism will produce a post-prior symmetry for four-body collisions, for which the (Coulomb) Born approximation is not symmetrical, remains to be seen.

It should be noted that there is a deeper significance to the fact that the present *reaction* amplitude (67) was obtained from the *exchange* contribution, (60), to the (elastic and inelastic) *scattering* amplitude, $(\alpha X|H|\beta X')$, of (57). In fact, the physical significance of the exchange aspect of (60) is that the outgoing proton is "not the same nucleon" as the incoming one, the free and bound protons having changed places during the collision. This amounts essentially to a reactive process, so it is hardly surprising that expression (60) can be promoted to a truly reactive matrix element by promoting an "effective" difference between the incoming and outgoing free particles to a true difference through use of an isotopic spin formalism.

ACKNOWLEDGMENTS

This work was supported by the Alexander von Humboldt Stiftung and the Max Planck Society, for which one of us (M.D.G.) is most grateful (and who would like to thank Professor O.E. Polanski, Director at the Max-Plank-Institut fur Strahlenchemie, for hospitality extended during the visits there); by the U.S. Office of Naval Research (for work carried out at the University of Oregon); and was done while the other (J.C.S.) was a guest scientist conducting research through the National Research Council–NASA Research Associateship Program.

APPENDIX

The enlarged Fock space on which the transformation (11) acts is the graded direct product[5,8] of the physical Fock space by an "ideal composite" space generated by the $\hat{a}_\mu^\dagger$ operators. Physically allowed states $|\psi\rangle$ in this enlarged space are sums of products of the $\hat{\psi}'s$, so that the new modes on which the $\hat{a}_\mu$ and $\hat{a}_\mu^\dagger$ operators act are unoccupied. Equivalently, physical states satisfy the subsidiary condition[3-7]

$$\hat{a}_\alpha|\psi\rangle = 0 \quad \forall\alpha\,, \tag{A1}$$

which is, in turn, equivalent to

$$\hat{N}_a|\psi\rangle = 0 \tag{A2}$$

with

$$\hat{N}_a = \sum_\alpha \hat{a}_\alpha^\dagger\, \hat{a}_\alpha \tag{A3}$$

the ideal-composite occupation-number operator. If $|\psi\rangle$ is a single-composite state $|\alpha\rangle = \hat{A}_\alpha^\dagger\,|0\rangle$ then it satisfies (A3) trivially since $\hat{a}_\alpha$ commutes or anticommutes with the $\hat{\psi}^\dagger$ fields,[3-7] in (7). The Fock-Tani image of such a state is[3-7] $|\psi) = \hat{U}^{-1}|\psi\rangle$ and satisfies the transformed subsidiary condition

$$\hat{U}^{-1}\,\hat{N}_a U|\psi) = 0 \tag{A4}$$

which will be satisfied if

$$\hat{a}_\alpha\hat{U}|\psi) = 0\,. \tag{A5}$$

States with one composite and no free constituents satisfy (A4) trivially.[3-7] More generally, states with one or more composites and/or free constituents can be shown[3-7] to satisfy (A4) provided that the composite wave functions are mutually nonoverlapping and also do not overlap the wave functions of any unbound constituents. This is the case for asymptotic initial and final states for few-body collisions built from asymptotically nonoverlapping (infinitely separated) wave packets. This standard interpretation of asymptotic states, and hence the triviality of the subsidiary condition, break down in the case of a macroscopic system of nonzero density, since any attempt to make all particle separations infinite (asymptotic limit) reduces the density to zero.

In such a nonzero-density system one can define *nonionic* states as arbitrary linear combinations of ideal-composite product states

$$|\alpha_1\alpha_2\cdots\alpha_n) = \hat{a}^\dagger_{\alpha_1}\,\hat{a}^\dagger_{\alpha_2}\cdots\hat{a}^\dagger_{\alpha_n}|0\rangle\ . \tag{A6}$$

The vacuum is invariant under $\hat{U}$,

$$\hat{U}|0\rangle = |0\rangle\ , \tag{A7}$$

because $\hat{F}$ of Sec. III annihilates the vacuum. It follows that (A5) can be rewritten using (A6),

$$\hat{a}_\alpha\hat{G}_{\alpha_1}\hat{G}_{\alpha_2}\cdots\hat{G}_{\alpha_n}|0\rangle = 0 \tag{A8}$$

where by (29)

$$\hat{G}_\mu \equiv \hat{U}\,\hat{a}^\dagger_\mu\,\hat{U}^{-1} = \hat{a}^\dagger_\mu\left(-\frac{\pi}{2}\right) = A^\dagger_\mu - \tfrac{1}{2}\sum_\nu \hat{A}^\dagger_\nu\,\hat{C}^p_{\nu\mu}\ . \tag{A9}$$

To lowest order in the G's, it can be seen that the Fock-space images $|\alpha_1..\alpha_n\rangle$ of states (A6) are just physical composite states $\hat{A}^\dagger_{\alpha_1}\cdots\hat{A}^\dagger_{\alpha_n}|O\rangle$. These product states contain only bound composites (no free constituents), hence the name "nonionic." Additional, more complicated terms[3–7] in $|\alpha_1\cdots\alpha_n\rangle$ become important when the composite wave functions overlap appreciably, in which case[5] $|\alpha_1\cdots\alpha_n)$ satisifes (A4), and hence $|\alpha_1\cdots\alpha_n\rangle$ satisfies (A2), only if the generator contains the new terms (21) and, even in this case, only to third order in wave functions. This can be seen in (A9) which is independent of the creation operators $\hat{a}^\dagger_\mu$. Because of the absence of $\hat{a}^\dagger_\mu$ in (A9) $\hat{a}_\alpha$ commutes through the G's in (A8) to annihilate the vacuum. In fact, the condition that G be independent of $\hat{a}^\dagger_\mu$ is a condition that can be used to solve for $\hat{U}$, (11).

Thus, the new terms in the generator that led to the cancellation of the secular terms in the solutions of each $\hat{a}^\dagger_\mu(t), \hat{A}^\dagger_\mu(t), \hat{\psi}(X,t)$, and $\hat{\psi}(x,t)$ also lead to satisfaction of the subsidiary condition to third order in wave functions. The new result should allow Fock- Tani representation, with all of its benefits, to be applied to problems involving composites in media of nonzero density.

[1] Gy. Csank, H.S. Taylor, and R. Yaris, Adv. At. Mol. Phys. **7**, 287 (1971).
[2] Gy. Csank, H.S. Taylor, and E. Ficocelli Varracchio, J. Chem. Phys. **61**, 263 (1974).
[3] M.D. Girardeau, Phys. Rev. Lett. **27**, 1416 (1971).
[4] M.D. Girardeau, J. Math. Phys. **16**, 1901 (1975).
[5] M.D. Girardeau and J.D. Gilbert, Physica **97A**, 42 (1979).
[6] M.D. Girardeau, Physica **98A**, 139 (1979).
[7] M.D. Girardeau, Int. J. Quantum Chem. **17**, 25 (1980).
[8] M.D. Girardeau, Phys. Rev. A **26**, 217 (1982).
[9] P.C. Ojha, M.D. Girardeau, J.D. Gilbert, and J.C. Straton, Phys. Rev. A **33**, 112 (1986).
[10] J.C. Straton and R. J. Drachman, in Proceedings of the Workshop on Annihilation in Gases and Galaxies, Greenbelt, MD, 1989, edited by Richard J. Drachman (NASA Conference Publications, Greenbelt, MD, in press).
[11] G.W. McClure, Phys. Rev. **148**, 47 (1966).
[12] P.J. Martin *et al.*, Phys. Rev. A **23**, 3357 (1981).
[13] J.D. Jackson and H. Schiff, Phys. Rev. **89**, 359 (1953).
[14] C.J. Joachain, *Quantum Collision Theory* (North-Holland, Amsterdam, 1983), p. 368.
[15] K.B. Choudhury, A. Mukherjee, and D.P. Sural, Phys. Rev. A **33**, 2358 (1986).
[16] B.H. Bransden, Adv. At. Mol. Phys. **1**, 85 (1965); see p. 95.
[17] M.R.C. McDowell and J.P. Coleman, *Introduction to the Theory of Ion-Atom Collisions* (North-Holland, Amsterdam, 1970), p. 381.
[18] E. Ficocelli Varracchio, Int. J. Quantum Chem. **27**, 11 (1985).
[19] D.S. Hughes and C. Eckart, Phys. Rev. **36**, 694 (1930); H.A. Bethe and E.E. Salpeter, *Quantum Mechanics on One- and Two-Electron Atoms* (Springer-Verlag, Berlin, 1959), pp. 166–170; M.D. Girardeau, Phys. Rev. A **28**, 3635 (1983).
[20] A.L. Fetter and J.D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971).
[21] See Appendix C in Ref. 4.
[22] S. Weinberg, Phys. Rev. **131**, 40 (1963).
[23] R. Shakeshaft and J.M. Wadehra, Phys. Rev. A **22**, 968 (1980).
[24] C. Sinha, S. Tripathi, and N.C. Sil, Phys. Rev. A **34**, 1026 (1986).
[25] J. Burgdorfer and K. Taulbjerg, Phys. Rev. A **33**, 2959 (1986).