Close-Coupling Symmetrized Variational Continuum Distorted-Wave Theory: Electron Capture to Excited States in *p*-H Collisions

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We present the first results of an *ab initio* coupled-channel calculation of electron capture to the $n = 2$ states of hydrogen in proton-hydrogen collisions using symmetrized variational (SV) continuum distorted-wave (CDW) theory. In SVCDW theory the collision ansatz includes both outgoing- and incoming-wave components in the wave functions, and represents in a compact and elegant form a very complete basis set for describing the electron capture process. We calculate total cross sections for nonresonant capture to the $2s$ and $2p$ states of the projectile, in the energy range 7–150 keV. The results are a substantial improvement over a previous variational CDW theory, and in particular are found to be in good accord with the available experimental data.

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Symmetrized variational continuum distorted-wave (SVCDW) theory has recently been formulated [1], and applied successfully to $1s \rightarrow 1s$ resonant electron capture in proton-hydrogen collisions. In SVCDW theory the general one-electron capture process for a target (projectile) of charge Z_T (Z_P) is described by a collision ansatz which includes a linear combination of incoming and outgoing continuum distorted waves (CDWs). These outgoing and incoming components of the wave functions are augmented by time-dependent phases chosen in such a way as to satisfy the long-range Coulomb boundary conditions; that is, they ensure that the initial (final) wave function has a Coulomb distortion appropriate to the asymptotic two-body system Z_P (Z_T), $Z_T - 1$ ($Z_P - 1$). Using this ansatz, the close-coupling quantal equations of motion are derived from a variational principle, thereby ensuring unitarity, detailed balancing, and gauge invariance of the theory. In the homonuclear case (that is, $Z_T = Z_P$), the SVCDW wave functions have the additional properties of well-defined parity and time symmetries [1]; indeed SVCDW theory is an exact CDW analog of undistorted traveling atomic orbital theory [2–4].

The inclusion of both outgoing and incoming waves in the SVCDW ansatz is designed to make the basis set more complete by simulating the dynamical molecular processes that are present during the collision when the two heavy particles are close together. In Ref. [1] we examined $1s \rightarrow 1s$ resonant electron capture in *p*-H collisions using a two-state SVCDW model. In comparison with previous variational CDW (VCDW) models, it was shown that for small and intermediate impact parameters the capture probability was greatly increased particularly at energies below 100 keV. This increase in probability was manifest in the $1s \rightarrow 1s$ capture cross sections, which, when multiplied by 1.202 to estimate empirically the contribution to capture from $n \geq 2$, were in good accord with experimental data for capture to all states. Resonant electron capture is however, a relatively easy process to model both from the point of view of theory and numerical tractability. In particular, when only the ground state of the target and the projectile are included in the calculation, the gerade and ungerade transition amplitudes admit analytic solutions [1].

It is the purpose of this Letter to further investigate the versatility of the SVCDW ansatz by performing a coupled-channel SVCDW calculation of total cross sections for capture to the $n = 2$ states of the projectile. These nonresonant processes are a much better test of the SVCDW ansatz, particularly the $1s \rightarrow 2s$ case, for which the total cross section shows a peak at about 25 keV. The calculations are also more demanding numerically, due to the fact that in both gerade and ungerade symmetries the transition amplitudes are strongly coupled even at large internuclear separations. Included in these new coupled-channel calculations are the $n = 1$ and $n = 2$ states of both the target and the projectile, with the axis of quantization for the p states taken along the internuclear vector [3]. This basis set is sufficient for a theoretical calculation of total electron capture to the projectile since the contribution from the $n = 3$ states is an order of magnitude less than that from $n = 2$ at the energies considered. To our knowledge the results presented in this Letter are the first truly coupled-channel CDW calculations.

For the purposes of this Letter then, we consider the homonuclear one-electron capture process

$$P^{Z+} + T^{(Z-1)^+}(1s) \longrightarrow P^{(Z-1)^+}(1s, 2s, 2p) + T^{Z^+}$$

in which a projectile (P) of charge Z, velocity $\mathbf{v}$, and impact parameter $\mathbf{b}$ impinges upon a hydrogenic target (T), also of charge Z, in the ground state, with the result that the electron is captured into the $n = 1, 2$ states of the projectile. To describe this process we take as the total

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wave function

$$\Psi = \sum_{k=1}^{4} [b_k(t)\Phi_k^T + b_{k+4}(t)\Phi_{k+4}^P],$$

where $b_k(t)$ are time-dependent coefficients whose optimum values are determined by the Sil variational principle [5], and

$$\Phi_k^T = \frac{1}{2}[\mathcal{E}_{Tk}^+ + (vb)^{+2iZ^2/v}\mathcal{E}_{Tk}^-], \quad (1)$$

$$\Phi_{k+4}^P = \frac{1}{2}[\mathcal{E}_{Pk+4}^- + (vb)^{-2iZ^2/v}\mathcal{E}_{Pk+4}^+], \quad (2)$$

where

$$\mathcal{E}_{Tk}^{\pm} = \xi_{Tk}^{\pm}\exp[i\arg(D_{\mathbf{v}}^{\mp}(\nu,\mathbf{R}))],$$
$$\mathcal{E}_{Pk+4}^{\pm} = \xi_{Pk+4}^{\pm}\exp[i\arg(D_{\mathbf{v}}^{\mp}(\nu,\mathbf{R}))],$$

and $\xi_{Tk}^{\pm}$, $\xi_{Pk+4}^{\pm}$ are the usual continuum distorted waves, that is,

$$\xi_{tK}^{\pm} = E_{k,\mathbf{v}}^T \exp\left[\pm i\frac{Z^2}{v}\ln(vR \mp v^2 t)\right] D_{-\mathbf{v}}^{\pm}(\nu,\mathbf{r}_P), \quad (3)$$

$$\xi_{Pk+4}^{\pm} = E_{k+4,-\mathbf{v}}^P \exp\left[\pm i\frac{Z^2}{v}\ln(vR \mp v^2 t)\right] D_{\mathbf{v}}^{\pm}(\nu,\mathbf{r}_T). \quad (4)$$

In Eqs. (3) and (4)

$$D_{\mathbf{u}}^{\pm}(\nu,\mathbf{r}) = e^{\pi\nu/2}\Gamma(1 \mp i\nu)_1F_1(\pm i\nu;1;\pm iur - i\mathbf{u}\cdot\mathbf{r})$$

are the normalized outgoing (+) and incoming (−) continuum distorted waves, and

$$E_{k',\mathbf{u}}^{\Gamma} = \phi_{k'}^{\Gamma}(\mathbf{r}_\Gamma)\exp\left[\frac{i}{2}\mathbf{u}\cdot\mathbf{r} - \frac{i}{8}v^2 t - i\epsilon_{k'}^{\Gamma} t\right]$$

is a traveling atomic orbital with $\phi_{k'}^{\Gamma}(\mathbf{r}_\Gamma)$ a hydrogenic bound-state orbital centered on the target (projectile) when $\Gamma = T$ (P). The coordinates $\mathbf{r}_T$ and $\mathbf{r}_P$ have their usual meanings within the impact parameter picture, with the internuclear vector $\mathbf{R}(t) = \mathbf{b} + \mathbf{v}t$ and $\nu = Z/v$.

With the row vector of VCDW wave functions,

$$\boldsymbol{\xi}^{\pm} = (\xi_{T1}^{\pm}, \xi_{T2}^{\pm}, \xi_{T3}^{\pm}, \xi_{T4}^{\pm}, \xi_{P5}^{\pm}, \xi_{P6}^{\pm}, \xi_{P7}^{\pm}, \xi_{P8}^{\pm}),$$

where the $\xi_k^{\pm}$ are given by Eqs. (3) and (4), and the corresponding row vector of SVCDW wave functions

$$\boldsymbol{\Phi} = (\Phi_1^T, \Phi_2^T, \Phi_3^T, \Phi_4^T, \Phi_5^P, \Phi_6^P, \Phi_7^P, \Phi_8^P),$$

where the Φ_k are given by Eqs. (1) and (2), we define the matrices $\mathbf{S}^{\pm}$ and $\mathbf{K}^{\pm}$ of VCDW matrix elements,

$$\mathbf{S}^{\pm\pm}(t) = \frac{1}{4}\langle\boldsymbol{\xi}^{\pm}\,|\,\boldsymbol{\xi}^{\pm}\rangle,$$

$$\mathbf{K}^{\pm\pm}(t) = \frac{1}{4}\langle\boldsymbol{\xi}^{\pm}|H - i\frac{d}{dt}|\boldsymbol{\xi}^{\pm}\rangle,$$

and similarly the matrices $\mathbf{S}$ and $\mathbf{K}$ of SVCDW matrix elements

$$\mathbf{S}(t) = \langle\boldsymbol{\Phi}\,|\,\boldsymbol{\Phi}\rangle,$$

$$\mathbf{K}(t) = \langle\boldsymbol{\Phi}|H - i\frac{d}{dt}|\boldsymbol{\Phi}\rangle.$$

Hence, by defining the matrices

$$\mathbf{P}(t) = \mathbf{S}^{++}(t) + e^{2i\theta}\mathbf{S}^{-+}(t),$$
$$\mathbf{Q}(t) = \mathbf{K}^{++}(t) + e^{2i\theta}\mathbf{K}^{-+}(t).$$

where

$$\theta \equiv \theta(t) = \arg[D_{\mathbf{v}}^{\mp}(\nu,\mathbf{R}(t))],$$

we may express $\mathbf{S}$ and $\mathbf{K}$ in terms of $\mathbf{S}^{\pm}$ and $\mathbf{K}^{\pm}$ and, thus,

$$\mathbf{S}(t) = \mathbf{P}(t) + \boldsymbol{\epsilon}_1\mathbf{P}^*(-t)\boldsymbol{\epsilon}_1,$$
$$\mathbf{K}(t) = \mathbf{Q}(t) + \boldsymbol{\epsilon}_1\mathbf{Q}^*(-t)\boldsymbol{\epsilon}_1 + \dot{\theta}(t)\mathbf{P}(t) - \dot{\theta}(-t)\boldsymbol{\epsilon}_1\mathbf{P}^*(-t)\boldsymbol{\epsilon}_1.$$

Finally, taking into account the rotation of the quantization axes

$$\mathbf{K}'(t) = \mathbf{K}(t) + i\frac{vb}{R^2}\mathbf{S}(t)\boldsymbol{\epsilon}_2,$$

where the matrices $\boldsymbol{\epsilon}_1$ and $\boldsymbol{\epsilon}_2$ may be written in terms of elementary matrices, thus,

$$(\boldsymbol{\epsilon}_1)_{ij} = \delta_{i,j} - 2(\delta_{i,4} + \delta_{i,8}),$$
$$(\boldsymbol{\epsilon}_2)_{ij} = \delta_{i-1,3} - \delta_{i+1,4} + \delta_{i-1,7} - \delta_{i+1,8},$$

where $\delta_{i,j}$ is the Kronecker delta function.

From Sil, the close-coupling quantal equations of motion are given by

$$i\mathbf{S}\dot{\tilde{\mathbf{b}}} = \mathbf{K}'\tilde{\mathbf{b}}, \quad (5)$$

where a tilde denotes transposition and a dot differentiation with respect to time. Because of the non-Hermitian nature of the matrix $\mathbf{K}'$ these equations are rendered numerically tractable by using Löwdin-Wannier symmetric orthonormalization [6] which uses the transformation

$$\psi = \hat{\boldsymbol{\Phi}}\langle\hat{\boldsymbol{\Phi}}\,|\,\hat{\boldsymbol{\Phi}}\rangle^{-1/2},$$

(where the caret denotes normalization of the basis set as a function of b and t) to transform the set of coupled equations (5) into the new set

$$i\dot{\tilde{\mathbf{c}}} = \mathbf{H}\tilde{\mathbf{c}}$$

in which $\mathbf{H}$ is Hermitian.

In order to highlight the success of the SVCDW ansatz we present our results in conjunction with those of a corresponding full-house VCDW calculation, in which the basis is taken to be the set of outgoing CDWs included in Eqs. (3) and (4); that is, outgoing CDWs are used for the entire heavy-particle trajectory [7]. Although concentrating on nonresonant capture, it is opportune at this point to comment upon $1s \rightarrow 1s$ resonant capture. Cross sections for resonant capture with the eight-state basis are increased by 7% at most over those calculated

in the two-state case. This demonstrates the stability of SVCDW as more states are added to the basis. The ratio of the present $n = 2$ capture results to those of two-state resonant capture shows an additional enlargement up to a maximum of 37% at 40 keV. At 10 keV the ratio is 15% and at asymptotically high (nonrelativistic) energies it is 12.5% in line with Oppenheimer scaling, namely, n^{-3} with $n = 2$. The result of this is that the theoretical predictions of the present eight-state SVCDW model for total capture are in very good agreement with experiment, and in particular lie within the experimental error bars.

Figure 1 shows the total cross sections for the process

$$H^+ + H(1s) \longrightarrow H(2s) + H^+.$$

Clearly full-house VCDW fails to model this process well at energies below 200 keV, where the two theoretical curves coalesce. The improvement of the SVCDW model over the full-house VCDW model is dramatic, and successfully predicts the turnover in the cross section at about 25 keV. We note that the SVCDW results agree very well with the highest energy points of the Bayfield [8] and Ryding, Wittkower, and Gilbody [9] experiments, thus minimizing any discrepancies due to a lack of normalization of the experimental data. Other theoretical close-coupling calculations give similarly good agreement with experiment; see the recent review by Fritsch and Lin [10]. To achieve this agreement, however, many of these calculations utilize large basis sets including the use of pseudostates on both target and projectile, which often embrace overcompleteness. We emphasize the *ab initio* nature of our calculations. For reasons of clarity we have not shown other theoretical calculations in the figure.

Figure 2 shows total cross sections for the process

$$H^+ + H(1s) \longrightarrow H(2p) + H^+.$$

In this case full-house VCDW tends to overestimate the cross sections by a factor of around 3 once the impact energy is below about 20 keV. Also the cross section appears to continue increasing as the energy decreases, in contradistinction to the experimental results. Once again the SVCDW results show a marked improvement, with the curve flattening off in line with experiment, although clearly there appears to be an almost constant discrepancy between SVCDW theory and experiment across virtually the entire range of the experimental results. It is difficult in this case to gauge how this discrepancy may be affected by a lack of normalization of the experimental data, since the highest available experimental point is at about 30 keV. We simply note that the SVCDW results are in almost perfect agreement with the experiment of Morgan, Geddes, and Gilbody [13] if we renormalize at 30 keV. Other theoretical calculations again give similarly good agreement with experiment. Nevertheless, in the energy range 7–30 keV other theory also tends to lie above experiment by amounts similar to that shown in Fig. 2; see, for example, Fig. 3.3 in [10]. The normalization of experiments [14] and [15] are based on measurements of Lyman-α excitation in e-H collisions which are in turn normalized to the first Born approximation at 1000 and 300 eV, respectively. That of [13] is based on a measurement of a $2p$ capture cross section at 18 keV in H^+-H_2 which is normalized to an absolute cross section of Lyman-α production in H^+-Ne . As seen in Fig. 2 all three experiments are in good accord with each other, and the question of a possible lack of normalization in the experimental results must remain an open one.

In conclusion, we have shown that SVCDW theory gives results which are in agreement with experiment for the reactions described above. This is in marked contrast to full-house VCDW which fails to reproduce experiment once the impact velocity is at or below the average velocity of the electron in the ground state. We attribute this to the more complete SVCDW basis set which lifts the outgoing- and incoming-wave degeneracy by including components of both in the wave functions.

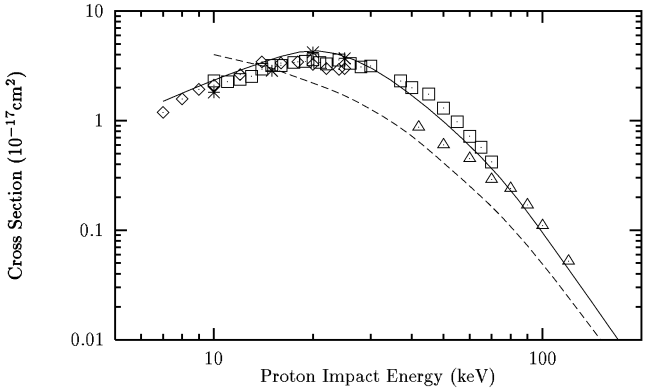

FIG. 1. Total cross sections (10^{-17} cm^2) for 1s to 2s electron capture by protons from atomic hydrogen vs proton impact energy E (keV) for SVCDW (solid curve) and full-house VCDW (dashed curve). Experimental results: Ref. [8] □, Ref. [11] ◇, Ref. [9] △, and Ref. [12] ∗.

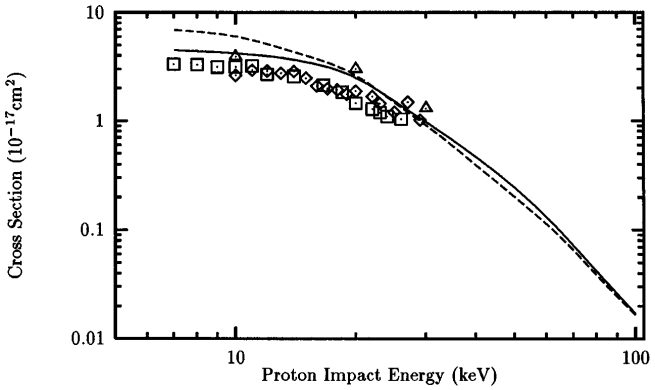

FIG. 2. Total cross sections (10^{-17} cm^2) for 1s to 2p electron capture by protons from atomic hydrogen vs proton impact energy E (keV) for SVCDW (solid curve) and full-house VCDW (dashed curve). Experimental results: Ref. [13] □, Ref. [14] ◇, and Ref. [15] △.

In this way a very complete basis set is achieved without the use of pseudostates and their attendant problems [16]. We have also shown that coupled-channel SVCDW theory is capable of reproducing experiment at lower impact energies than might previously have been thought, while at the same time guaranteeing correct behavior of the cross sections when the impact velocities are asymptotically (but nonrelativistically [17] large). In a real sense then, SVCDW theory represents a synthesis of the molecular orbital (MO) and the atomic orbital (AO) approaches by including the best characteristics of both (see [10] for a fuller discussion of MO and AO techniques). A definite conclusion on this point awaits further theoretical work; currently calculations involving heteronuclear collisions are being carried out. The present work also bridges a gap that has always existed in the theory of heavy-particle rearrangement collisions, between CDW models based on perturbation theory, on the one hand, and large coupled-channel calculations (including pseudostates), on the other hand.

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[1] G. J. N. Brown and D. S. F. Crothers, J. Phys. B **27**, 5309 (1994).
[2] R. McCarroll, Proc. R. Soc. London A **264**, 547 (1961).
[3] L. Wilets and D. F. Gallagher, Phys. Rev. **147**, 13 (1966).
[4] I. M. Cheshire, G. H. Gallagher, and A. Taylor, J. Phys. B **3**, 813 (1970).
[5] N. C. Sil, Proc. Phys. Soc. London **57**, 194 (1960).
[6] D. S. F. Crothers, Nucl. Instrum. Methods Phys. Res., Sect. B **27**, 555 (1987).
[7] D. S. F. Crothers and J. F. McCann, J. Phys. B **18**, 2907 (1985).
[8] J. Bayfield, Phys. Rev. **185**, 105 (1969).
[9] G. Ryding, A. B. Wittkower, and H. B. Gilbody, Proc. Phys. Soc. London **89**, 547 (1966).
[10] W. Fritsch and C. D. Lin, Phys. Rep. **202**, 1 (1991).
[11] J. Hill, J. Geddes, and H. B. Gilbody, J. Phys. B **12**, L341 (1979).
[12] Y. P. Chong and W. L. Fite, Phys. Rev. A **16**, 933 (1977).
[13] T. J. Morgan, J. Geddes, and H. B. Gilbody, J. Phys. B **6**, 2118 (1973).
[14] T. Kondow, R. J. Girnius, W. P. Chong, and W. L. Fite, Phys. Rev. A **10**, 1167 (1974).
[15] R. F. Stebbings, R. A. Young, C. L. Oxley, and H. Ehrhardt, Phys. Rev. A **138**, 1312 (1965).
[16] H. A. Slim and A. M. Ermolaev, J. Phys. B **27**, L203 (1994).
[17] Of course relativistic CDW theories exist; see, for example, J. G. Glass, J. F. McCann, and D. S. F. Crothers, J. Phys. B **27**, 3445 (1994).