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LETTER TO THE EDITOR

Resonant electron–hydrogen atom scattering using hyperspherical coordinate method

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Abstract. *The scattering of unpolarized electrons from hydrogen atoms is treated using* the hyperspherical coordinate and the multichannel quantum defect approach with particular emphasis on the formation of quasi-stable resonant e^-–H complexes. Resonant positions and widths, formed below the H($n = 2$), H($n = 3$), and H($n = 4$) thresholds, are calculated for symmetries $^{1,3}S^e$, $^3P^o$, and $^1D^e$. Resonant cross sections are also given for the singlet and triplet $L = 0$ partial waves. Good agreement is found with other more computationally intensive calculations.

Electron–hydrogen scattering forms the most basic of all three-body atomic collisions. Many elaborate methods have been proposed and implemented covering the range of electron energies from thermal energies to hundreds of eV above the ionization limit. Close-coupling expansion using pseudostates (Burke *et al* 1963, Callaway and Wotten 1974, Morgan *et al* 1977, Callaway 1982, 1985) and R-matrix (Scholz *et al* 1988, Pathak *et al* 1988) methods have yielded accurate numerical values for the elastic and inelastic cross sections including resonance parameters. Other numerical methods, while not providing non-resonant information such as cross sections, have calculated positions and widths of these resonant states for this two-electron system (Ho and Callaway 1986, Ho 1990).

This letter reports on a calculation of scattering cross sections and resonant positions and widths for incident electron energies sufficient for excitation of H($n = 2$), H($n = 3$), and H($n = 4$) states using the non-adiabatic hyperspherical coordinate representation (HSC) and the multichannel quantum defect theory (MQDT). The utility of the HSC coordinates has been most effectively demonstrated over the past two decades in the classification and identification of the doubly-excited resonant states of two-electron species such as H^- and He (Macek 1968, Lin 1974, 1986, Koyoma *et al* 1986). In Macek's adiabatic HSC treatment (Macek 1968), the HSC Hamiltonian is parametrized in the 'slow' coordinate $R = (r_1^2 + r_2^2)^{1/2}$ in analogy with the adiabatic Born–Oppenheimer approximation for diatomic molecules. Recent studies using this adiabatic representation have been able to identify the dominant excitation and photoabsorption channels for the photodetachment and photoionization of H^- and He (Sadeghpour and Greene 1990, Sadeghpour 1991).

In this work, the non-adiabatic radial coupling terms responsible for the excitation of different hydrogenic manifolds are taken into account by numerical propagation

of a set of coupled equations in R outward to a matching radius $R = R_0$ in the asymptotic region, beyond which the radial couplings are ignored. Radial solutions in the inner region are mapped onto the asymptotic solutions which are assumed valid for all $R \geqslant R_0$. Scattering parameters weakly dependent on energy are obtained within the framework of MQDT (Seaton 1966, 1982, Greene *et al* 1979, Greene and Jungen 1985). These parameters are then interpolated on a fine energy mesh for the calculation of scattering phaseshifts and cross sections exhibiting rich resonance structure.

The calculations presented here are performed in two stages. First, adiabatic hyperspherical potential curves and associated couplings are obtained. To this end, the total operator $\hat{U}(R;\Omega) = [\Lambda^2/2R^2 + C(\alpha,\theta_{12})/R]$ is diagonalized at each R

$$\hat{U}(R;\Omega)\Phi_\mu(R;\Omega) = U_\mu(R)\Phi_\mu(R;\Omega). \tag{1}$$

In (1), $\alpha = \tan^{-1}(r_2/r_1)$ lies in the range 0 to $\pi/2$ and $\theta_{12} = \cos^{-1}(\hat{r}_2 \cdot \hat{r}_1)$ ranges from 0 to 2π, Λ^2 is the 'grand' angular momentum operator and $C(\alpha,\theta_{12})$ acts as an 'effective' charge for the three-body system. (Explicit expressions for these operators are given in Sadeghpour (1991).) The diagonalization of the fixed R Hamiltonian in (1) is done using a linear combination of non-orthogonal basis functions, $\Phi_\mu(R;\Omega) = \sum_i \phi_i(R,\Omega)c_{i\mu}(R)$, which includes eigenfunctions of the grand angular momentum operator augmented with two-electron basis functions constructed from properly symmetrized products of one-electron orbitals to represent the asymptotic channel functions. The resulting generalized eigenvalue equation $\mathbf{U}\mathbf{c}_\mu = U_\mu(R)\mathbf{O}\mathbf{c}_\mu$, in which $\mathbf{O}$ is the full overlap matrix between the basis functions, is solved to obtain accurate adiabatic potential energy curves and radial coupling elements, $P_{\mu\mu'}(R) = \langle\Phi_\mu|(\mathrm{d}/\mathrm{d}R)\Phi_{\mu'}\rangle$.

Next, excitation and non-radiative decay probabilities of the autodetaching states are calculated by the non-adiabatic coupling of these HSC potentials in

$$\left[\left(\mathbf{I}\frac{\mathrm{d}}{\mathrm{d}R} + \mathbf{P}(R)\right)^2 + 2(\mathbf{I}E - \mathbf{U}(R))\right]\mathbf{F}(R) = \mathbf{0} \tag{2}$$

where $\mathbf{I}$ denotes the identity matrix and the diagonal matrix $\mathbf{U}(R)$ contains the potential energies. The components of the solution matrix $F_{j\beta}(R)$ in each channel are propagated outward from the origin, subject to the boundary condition $F_{j\beta}(R) \to R^{\lambda_j+1}\delta_{j\beta}$ as $R \to 0$ where λ are the eigenvalues of the grand angular momentum operator, to the matching radius $R = R_0$. Here $j \equiv \{n,\mu\}$, where n is the hydrogenic principal quantum number and μ is the HSC channel function index. The Gordon stablilization procedure is used to ensure the linear independence of the solution vectors (Gordon 1967).

A shortcoming of the HSC representation is the 'artificial' behaviour of the channel coupling, $P_{\mu\mu'}(R) \sim R^{-1}$, at large R. This residual coupling has been shown by Macek (1985) to manifest itself in the phase of the out-going electron wavefunction such that at high energies the effect of this coupling on the phaseshift becomes large. An attempt at remedying this problem for the calculation of the elastic S-wave phaseshift involved matching the HSC wavefunctions to the close-coupling solutions in independent-electron coordinates (Christensen-Dalsgaard 1984). It will be shown here that a combined hyperspherical and quantum-defect treatment can adequately describe the long-range phenomena in terms of a few parameters typical to all MQDT analyses.

To this end, linear combinations of the solution vectors, $\boldsymbol{F}_\beta$, are expanded on the hypersphere at $R = R_0$, in terms of regular and irregular functions appropriate to the asymptotic region

$$\sum_{\beta=1}^{N} F_{j\beta}(R_0)c_{\beta\nu} = f_j(R_0)U_{j\nu}\cos(\pi\mu_\nu) - g_j(R_0)U_{j\nu}\sin(\pi\mu_\nu) \quad (3)$$

where $\nu = 1, \ldots, N_0$, with N_0 the number of open and weakly-closed (energetically inaccessible) channels, and N the total number of channels retained in (2). A similar equation also holds for the radial derivatives. f_j and g_j are the energy-normalized functions in each fragmentation channel j and are evaluated at $R = R_0$. These functions are oscillatory in the energetically accessible open channels and are exponentially divergent in the weakly-closed channels in which the resonances form. $U_{j\nu}$ are the orthogonal frame-transformation matrices connecting the eigenchannels ν and the detachment channels j and μ_ν are the eigenquantum defects common to each detachment (fragmentation) channel (Greene and Jungen 1985). In the strongly-closed channels the linear superposition of the inner solution vectors vanishes for $R \geqslant R_0$. Equation (3) can be transformed into

$$\Gamma c = \tan \pi\mu \Lambda c \quad (4)$$

where the matrices Γ and Λ contain the Wronskian of the left-hand side of (3) with f_j and g_j, respectively. The number of the eigenvalues of (4) will be the same as the number of open and weakly-closed channels, since Λ is of rank N_0. In this fashion, all the information about the short-range interaction of the incident electron with the hydrogen atom is embedded in $U_{j\nu}$ and $\pi\mu_\nu$. These parameters, which vary smoothly with energy, are used to construct the full scattering matrix in the usual MQDT manner (see Greene and Jungen 1985 for details). Elastic and inelastic cross sections are computed, enhanced by the presence of resonance structures. These resonances form in each HSC channel j where the outer electron experiences an attractive permanent dipole moment of the hydrogen atom, $a_j < -\frac{1}{4}$ (Gailitis and Damburg 1963, Seaton 1961). There are also repulsive dipole fragmentation channels ($a_j > -\frac{1}{4}$) which contribute only to the continuum excitation. The non-radiative decay width and the position of these resonances scale approximately as $\epsilon_{m+1}/\epsilon_m = \Gamma_{m+1}/\Gamma_m = \mathrm{e}^{-2\pi/\alpha_j}$ where $\alpha_j \equiv (-a_j - \frac{1}{4})^{1/2}$ and $m = n$ indexes the lowest member of any resonance series belonging to the $j \equiv \{n, \mu\}$ group. ϵ_m is the one-electron binding energy relative to the respective n-series limit and Γ_m is the full width at half maximum.

In figure 1(a) and (b), the 1s–1s $^3\mathrm{S}^\mathrm{e}$ and $^1\mathrm{S}^\mathrm{e}$ cross sections are given for incident electron energies near the H($n = 2$) threshold. Six HSC channels were included inside a 'box' of $R_0 = 25$ au for the result shown. The highest three channels were treated as strongly closed and a three-channel MQDT analysis was carried out on the reaction boundary. Also shown are the results of an R-matrix calculation by Scholz and Scott (1991). The resonance positions and widths below the $n = 2$ threshold, tabulated in table 1, were obtained from the maximum value of $2(\mathrm{d}\delta/\mathrm{d}E)^{-1}$, where δ is the short-range phaseshift of the electron in the open 1sϵl channel. This phaseshift displays rapid variation with energy as shown in figure 1(c). However, the eigenphaseshifts ($\pi\mu_\nu$) calculated with the MQDT method for the three open and weakly-closed channels do not show, in figure 1(d), this variation with energy. This

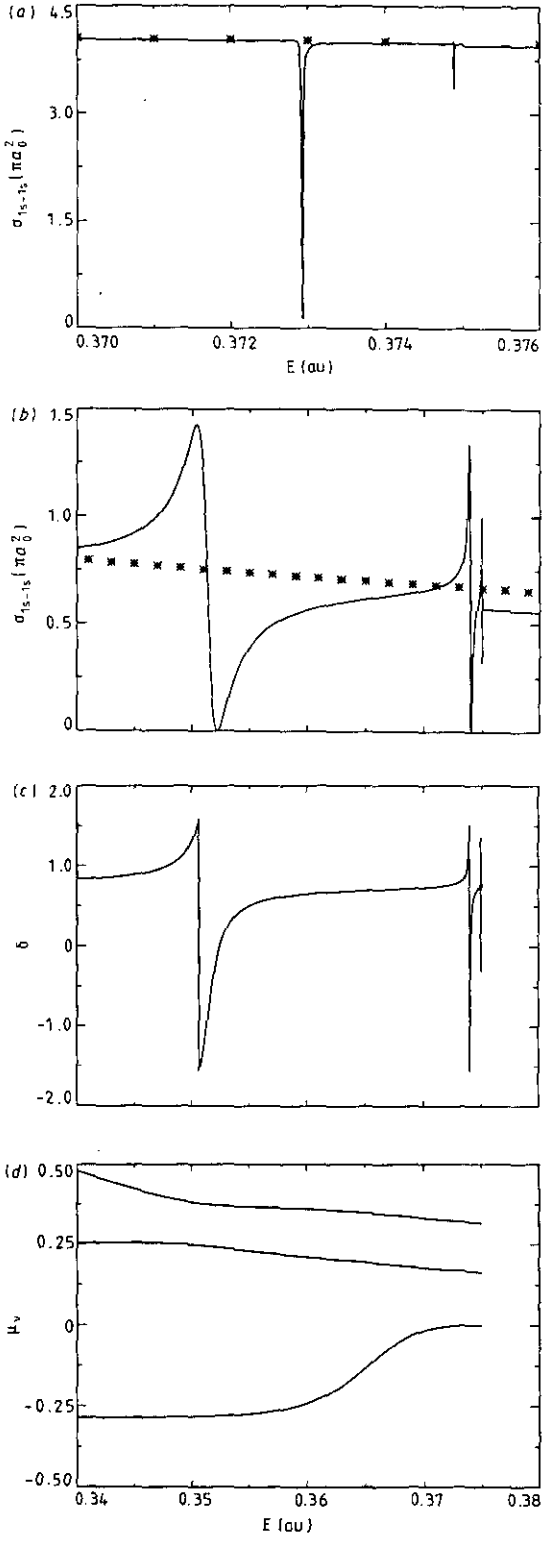

Figure 1. (*a*) *The elastic* 1*s*–1*s* $^3S^e$ *cross section* in πa_0^2 for incident electron energies (in atomic units) below the H(n =2) threshold, (*b*) $^1S^e$ cross section, (*c*) the elastic phase-shift δ in the 1sεs open channel exhibiting *resonance effect* and (*d*) the eigenquantum defects μ_ν for the three open and weakly-closed $^1S^e$ channels. The n = 2 *threshold* is at 0.375 au (1 au = 27.211 652 eV). The asterisks are the R-matrix calculation of Scholz and Scott (1991).

is the trademark of MQDT analysis which allows the numerically intensive short-range calculation inside the HSC box to be carried out for a few energies and the resulting parameters to be interpolated economically on any *desired* energy mesh so as to resolve even the narrowest structure in the cross section.

Table 1. Resonance energies (E) and widths (Γ) in eV. The Rydberg unit is 13.605826 eV.

$^{2S+1}L^{\pi}$	${}_n\{v\}^A_m$	$E(\Gamma)$ (present)	$E(\Gamma)$ (expt)	$E(\Gamma)$ (calculated)
$^1S^e$	${}_2\{0\}^+_2$	9.559(0.0475)	9.549(0.063)[g]	9.56(0.047)[a], 9.557(0.052)[b] 9.55735(0.047 17)[c], 9.5572(0.0471)[e]
	${}_2\{0\}^+_3$	10.176(0.0031)		10.178(0.0022)[a], 10.177(0.0026)[b]
	${}_3\{0\}^+_3$	11.731(0.0399)	11.7241[h]	11.7281(0.0389)[f], 11.728 05(0.040 95)[b]
	${}_3\{0\}^+_4$	12.030(0.0100)		12.033 67(0.008 313)[f], 12.033 71(0.007 891)[b]
	${}_4\{0\}^+_4$	12.525(0.0225)		12.528(0.0298)[b], 12.5272(0.025 85)[d]
	${}_4\{0\}^+_5$	12.693(0.008)		12.6936(0.007 35)[b], 12.6927(0.009 25)[d]
	${}_4\{1\}^+_4$	12.671(0.0195)		12.6618(0.019 32)[b], 12.6609(0.023 95)
$^3S^e$	${}_2\{0\}^-_2$	10.148(0.000 46)		10.150(2.0 × 10^{-5})[a], 10.147[b]
	${}_2\{0\}^-_3$	10.201(1.68 × 10^{-5})		
	${}_3\{0\}^-_3$	12.001(0.000 21)	12.0098[h]	12.0008(0.000 24)[f], 12.0008(0.000 23)[b]
	${}_3\{0\}^-_4$	12.075(4.1 × 10^{-5})		12.0754(5.82 × 10^{-5})[f], 12.07554[b]
$^1D^e$	${}_2\{0\}^+_2$	10.129(0.0101)	10.115(0.006)[g]	10.1253(0.008 81)[e], 10.126(0.0088)[b] 10.124 46(0.008 62)[i]
$^3P^o$	${}_2\{0\}^-_2$	9.745(0.007 65)	9.736(0.005)[g]	9.74(0.0059)[a], 9.7382(0.005 82)[e] 9.741(0.0071)[b], 9.7381(0.0058)[d]
	${}_3\{0\}^-_3$	11.771(0.0519)	11.7721[h]	11.7582(0.0435)[f], 11.7578(0.046 68)[b] 11.758 15(0.04354)[d]

[a] Taylor and Burke (1967). [b] Pathak *et al* (1988). [c] Ho *et al* (1977).
[d] Ho (1990). [e] Scholz *et al* (1988). [f] Callaway (1982).
[g] Warner *et al* (1986). [h] Warner *et al* (1990). [i] Bhatia and Ho (1990).

The 1s–1s cross section in the $^1S^e$ is shown in figure 2(*a*) for incident electron energies between the H($n = 2$) and H($n = 3$) thresholds. Seven HSC channels were included in (2) and a six-channel ($N_0 = 6$) MQDT analysis was carried out at $R_0 = 42$ au for the $^1S^e$ scattering parameters. The cross section reveals resonance structure converging on the $n = 3$ manifold of hydrogen.

These resonances are classified with the group theory quantum numbers of Herrick (1983) and Lin (1983) (K, T and A), which for the S-wave even-parity scattering take values of $T = 0$, $K = n-1, n-3, \ldots, -(n-3), -(n-1)$, and $A = (-1)^S$, with S the total spin. It has been shown for the photodetachment of H^- that a more appropriate quantum number is the 'bending' quantum number v^A (Sadeghpour and Greene 1990, Watanabe and Lin 1986) which for the $^1S^e$ and $^3S^e$ symmetries has values of $v^A = 0^+, 1^+, 2^+, \ldots$, and $v^A = 0^-, 1^-, 2^-, \ldots$, respectively. For instance, the lowest member of the resonance series converging to H($n = 3$) can be identified with the compact notations of ${}_n\{v\}^A_m = {}_3\{0\}^+_3$ and ${}_3\{0\}^-_4$, depending upon the spin. In this '+' state, the electrons interact strongly through the electron–electron interaction term and are therefore rapidly autodetaching (Cooper *at al* 1963). On the other hand, in the '–' state, the interaction is minimal leading to strong stability against autodecay as the electrons occupy different radial 'orbits'. Resonance

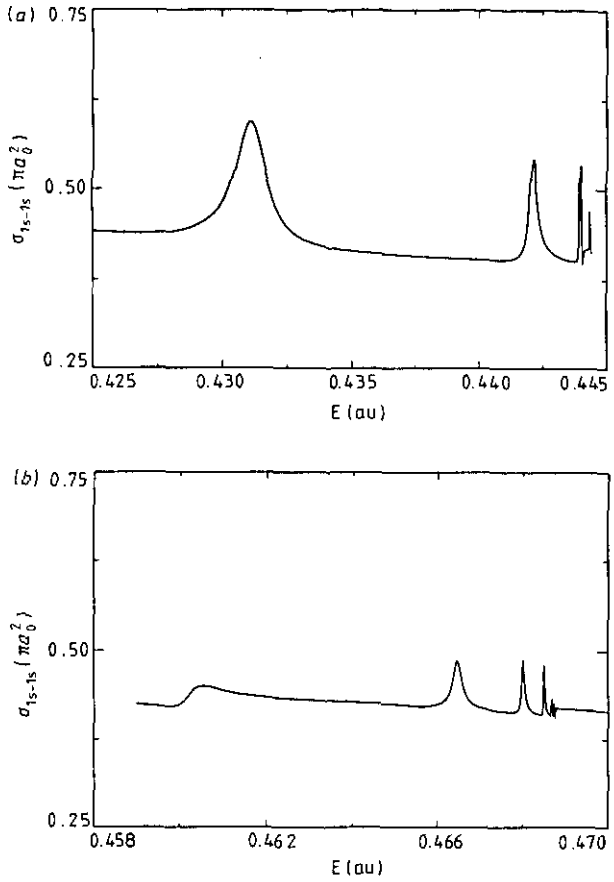

Figure 2. The $^1S^e$ elastic cross section for (*a*) electron energies near the H(n = 3) threshold at 0.444 44 au and (*b*) electron energies in the vicinity of the H(n = 4) threshold at 0.468 75 au.

parameters for symmetries $^3P^o$ and $^1D^e$ are also given in table 1 and are classified with the above notation.

In figure 2(*b*) the $^1S^e$ cross section for electron energies above the H(n = 3) threshold is presented displaying resonances converging to the series limit at H(n = 4). An eleven-channel HSC–MQDT calculation was performed at $R_0 = 63$ au for the results shown. For the $^1S^e$ symmetry, the $n = 4$ manifold is the first instance the electron can bind to more than *one* attractive dipole channel, namely the ${}_n\{v\}^A = {}_4\{0\}^+$ and ${}_4\{1\}^+$ channels. One should therefore expect two separate series of resonances identifiable with these quantum numbers. Indeed the first broad resonance is the lowest member of the ${}_4\{0\}^+$ series classified as a ${}_4\{0\}_4^+$ resonance and the next resonance has the quantum numbers ${}_4\{1\}_4^+$ belonging to the next attractive dipole channel ${}_4\{1\}^+$. The resonance parameters are provided in table 1 where good accord with other calculations is observed. The magnitude of the cross section also agrees reasonably well (to within 15%) with the calculations of Callaway and Wooten (1974) and the R-matrix calculation of Scholz and Scott (1991).

In conclusion, cross sections and resonant positions and widths have been obtained

for the e–H scattering in the combined hyperspherical coordinate and multichannel quantum defect approach. The results of this work confirm that this unified theory can successfully predict the formation of resonance structure in the scattering of electrons from hydrogen atoms.

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