Long-range states in excited ultracold
3He*–4He* dimers

D G Cocks1, G Peach2 and I B Whittingham1

1 College of Science, Technology and Engineering, James Cook University, Townsville 4811, Australia
2 Department of Physics and Astronomy, University College London, London WC1E 6BT, UK

E-mail: daniel.cocks@jcu.edu.au

Received 10 September 2014, revised 29 March 2015
Accepted for publication 1 April 2015
Published 28 April 2015

Abstract
Long-range bound states of the excited heteronuclear 3He*–4He* system that dissociate to either 3He(1s2s 3S1) + 4He(1s2p 3P) or 4He(1s2p 3P) + 3He(1s2s 3S1), where j = 0, 1, 2, are investigated using both single-channel and multichannel calculations in order to analyse the effects of Coriolis and non-adiabatic couplings. The multichannel calculations predict two groups of resonances above the lowest asymptotic energy. One of these groups dissociates to an atomic pair with the 2p excitation on the fermionic atom and the other dissociates to two asymptotes which correspond to the 2p excitation on either atom. Many of these resonances could be identified with levels in the single-channel calculation although the differences in energies were large. The total parity was found to have a significant influence on the ability to make these identifications. No purely bound states were found, although several resonances with line widths smaller than 1 MHz were obtained.

Keywords: cold gases, metastable helium, photoassociation, close-coupled calculations, scattering resonances

1. Introduction
A widely used technique to study the dynamics of ultracold collisions in dilute quantum gases is photoassociation in which two interacting ultracold atoms are resonantly excited by a laser to bound states of the molecule formed during the collision. Photoassociation in metastable rare gases is of particular interest since novel experimental strategies can be implemented. In contrast to ground-state atomic species which have been trapped at ultracold temperatures, the large internal energy of the metastable atom can allow experimentalists to easily detect individual events with high resolution and hence potentially count each atom which has ionized or escaped from the trap [1, 2].

Photoassociation of two bosonic metastable 4He* atoms, 4He(1s2s 3S1), to excited rovibrational bound states that dissociate to the 4He(1s2s 3S1) + 4He(1s2p 3P) limits, where j = 0, 1, 2, and of two fermionic metastable 3He* atoms, 3He(1s2s 3S1), to states that dissociate to 3He(1s2s 3S1) + 4He(1s2p 3P), have recently been theoretically investigated by Cocks et al [3, 4]. They use both single-channel and multichannel calculations based upon input molecular potentials constructed from the short-range ab initio 1,3,5Σ+ and 1,3,5Πu potentials of Deguilhem et al [6] matched onto long-range retarded resonance dipole and dispersion potentials. The multichannel calculations permitted criteria to be established for the assignment of the theoretical levels to experimental observations in the case of the bosonic system and, in the absence of any experimental observations of bound states in the fermionic system, predictions as to which of the calculated bound states may be experimentally observable.

The heteronuclear 3He*–4He* system has been relatively unexplored. The spin polarized mixture with 3He(1s2s 3S1) in the state (j, m_j) = (3/2, +3/2) and 4He(1s2s 3S1) in the state (j, m_j) = (1, +1) has been simultaneously magneto-optically trapped [7] and 4He* used to sympathetically cool 3He* to the quantum degenerate regime [8]. Goosen et al [9] have undertaken a theoretical investigation of Feshbach resonances in homonuclear and heteronuclear mixtures of 3He* and 4He*, predicting a broad resonance in the heteronuclear system. Recently, Borbely et al [10] have predicted that, as 3He*–4He* mixtures prepared in their lowest spin channel are stable against Penning ionization, they provide the ideal...
starting point for future experiments such as preparing an ultracold mixture in an optical dipole trap in order to study this Feshbach resonance.

We report here a theoretical investigation of the long-range bound states of the excited heteronuclear $^3$He*–$^4$He* system that dissociate to either $^3$He(1s2s $^3S_1$) + $^4$He(1s2p $^3P_j$) or $^3$He(1s2p $^3P_j$) + $^4$He(1s2s $^3S_1$), where $j = 0, 1, 2$. The structure of these states is expected to differ substantially from those found for the homonuclear systems as the large number of asymptotes available in the heteronuclear configuration means many of the bound states of a given channel will be embedded in a continuum of states of other channels and become resonances associated with predissociation. These states are relevant to any future studies of photoassociation in such mixtures and are investigated using both single-channel and multichannel calculations in order to analyse the effects of Coriolis and non-adiabatic couplings.

Atomic units are used, with lengths in Bohr radii $a_0 = 0.052$ 917 7209 nm and energies in Hartree $E_h = \alpha^2 m_e c^2 = 27.211$ 384 eV.

2. Theory

2.1. Multichannel equations

The formalism for the excited heteronuclear $^3$He*–$^4$He* system requires some modification of that presented by Cocks et al [4] for the excited homonuclear $^3$He*–$^3$He* system. In particular, there are fewer symmetries in the heteronuclear system that can be taken advantage of and we must be sure to include all coupled states, including those states possessing asymptotic forms with the excitation on either the fermionic or bosonic atom.

The total Hamiltonian for a system of two interacting atoms $i = 1, 2$ with reduced mass $\mu$, interatomic separation $R$ and relative angular momentum $I$, where both atoms possess fine structure and one hyperfine structure is

$$\hat{H} = \hat{T}_K + \hat{H}_{rot} + \hat{H}_{el} + \hat{H}_{hf},$$  

where $\hat{T}_K$ is the kinetic energy operator

$$\hat{T}_K = -\frac{\hbar^2}{2\mu R^2} \frac{\partial}{\partial R} \left( R^2 \frac{\partial}{\partial R} \right),$$  

and $\hat{H}_{rot}$ the rotational operator

$$\hat{H}_{rot} = \frac{\hat{J}^2}{2\mu R^2}.$$  

The total electronic Hamiltonian is

$$\hat{H}_{el} = \hat{H}_i + \hat{H}_j + \hat{H}_{ij},$$  

where $\hat{H}_i$ is the unperturbed Hamiltonian of atom $i$ and $\hat{H}_{ij}$ is the electrostatic interaction between the atoms. The terms $\hat{H}_{el}$ and $\hat{H}_{hf}$ in equation (1) describe the fine structure and hyperfine structure respectively of the atoms.

The multichannel equations describing the interacting atoms are obtained by writing the eigenvector $|\Psi\rangle$ of the total system, which satisfies

$$\hat{H}|\Psi\rangle = E|\Psi\rangle,$$

in terms of an expansion

$$|\Psi\rangle = \sum_{a} \frac{1}{R} G_a(R)|\alpha\rangle,$$

where $G_a(r)$ are vibrational wave functions and the molecular basis is $|\alpha\rangle = |\mathbf{R}_i, q, q_j\rangle$, where $q$ denotes the interatomic polar coordinates $(\theta, \phi)$ and electronic coordinates $(r_i)$. The state label, $\alpha$, denotes the set of approximate quantum numbers describing the electronic-rotational states of the molecule. We make the Born–Oppenheimer (BO) approximation that the basis states $|\alpha\rangle$ depend only parametrically on $R$ so that $|\alpha'\rangle |\mathbf{R}_K\rangle = 0$. In this approximation [5], the nuclear separation only enters the matrix elements through the molecular potentials of the electronic Hamiltonian $\hat{H}_e$ and the rotational Hamiltonian $\hat{H}_{rot}$. This implies the hyperfine-structure is $R$-independent and that the bulk of the $R$-dependence of $|\Psi\rangle$ is contained in the vibrational factors $G_a(R)$. We have previously used this approximation to achieve very good agreement between our calculations and the many experimental observations for the homonuclear $^3$He*–$^3$He* system [3]. We note that it is common to refer to BO states as adiabatic states in the absence of hyperfine structure and rotational couplings. In our case, the states $|\alpha\rangle$ are a unitary transformation from the set of BO states and we later refer to adiabatic states of the complete Hamiltonian neglecting the kinetic energy term, $\hat{H}_K$. Forming the scalar product $\langle \alpha' | \hat{H} | \Psi \rangle$ yields the set of multichannel equations

$$\sum_{a} \left[ -\frac{\hbar^2}{2\mu R^2} \frac{\partial^2}{\partial R^2} + V_{a\alpha}(R) - E\delta_{a\alpha} \right] G_a(R) = 0,$$

(7)

where

$$V_{a\alpha}(R) = \langle \alpha' | [\hat{H}_{rot} + \hat{H}_{el} + \hat{H}_{hf}] |\alpha\rangle.$$

(8)

2.2. Basis states and matrix elements

The excited heteronuclear $^3$He*–$^4$He* system can be in two possible arrangements: $^3$He(1s2s $^3S_1$) + $^4$He(1s2p $^3P_j$) and $^3$He(1s2p $^3P_j$) + $^4$He(1s2s $^3S_1$).

For notational convenience we shall assume both nuclei have angular momentum $\hat{I}_i$ and set the appropriate nuclear angular momentum to zero at the end of the formalism. If the two colliding atoms have orbital $\hat{L}_i$ and spin $\hat{S}_i$ angular momenta, the body-fixed eigenstates of total parity $\hat{P}_i$ for the two arrangements in the coupling scheme

$$\hat{J}_i = \hat{L}_i + \hat{S}_i, \quad \hat{J}_i = \hat{J} + \hat{I}_i, \quad \hat{\mathbf{F}} = \hat{\mathbf{J}} + \hat{\mathbf{I}},$$

are (see appendix A for details)

$$|\alpha\rangle_{12} \equiv \left\{ (\alpha_1)_A, (\alpha_2)_B, f, \phi, T, m_T, P_T \right\},$$

$$\equiv \left\{ (\gamma_1 j_1 i_1 f_1)_A, (\gamma_2 j_2 i_2 f_2)_B, f, \phi, T, m_T, P_T \right\}.$$
\[ |a \rangle_{21} = \left[ (\gamma_1)_{\Lambda}, (\gamma_2)_{\Lambda}, LS_{\Omega}, LS_{\phi}, \right], \]

\[ \equiv \left\{ (\gamma_2)_{\Lambda}, (\gamma_1)_{\Lambda}, f, \phi, T, m_T, P_T \right\}, \]

where \( \gamma \equiv \{ \bar{\gamma}, L_1, S_1, \} \), \( \bar{\gamma} \) representing any other relevant quantum numbers, and \( \phi \equiv \{ \Omega_f \} = \{ \Omega_f \} \). The nuclei of \(^3\)He and \(^4\)He are labelled \( A \) and \( B \) respectively and we define the intermolecular axis to be \( R = r_B - r_A \). The sets of quantum numbers \( (\gamma_1, j_1) \) and \( (\gamma_2, j_2) \) describe the 1s2s \(^3\)S\(_1\) and 1s2p \(^3\)P\(_2\) states respectively. The projections of an angular momentum \( J \) onto the space-fixed axis \( OZ \) and inter-molecular axis \( OZ \) with orientation \((\theta, \varphi)\) relative to the space-fixed frame are denoted \( m_J \) and \( \Omega_f \) respectively.

The alternative body-fixed states

\[ \left\{ (\gamma_1)_{\Lambda}, (\gamma_2)_{\Lambda}, f, \psi, \Omega_f, T, m_T, P_T \right\} \]

and

\[ \left\{ (\gamma_1)_{\Lambda}, (\gamma_2)_{\Lambda}, LS_{\Omega}, LS_{\phi}, \right\}, \]

arising from the couplings \( \bar{L} = L_1 + L_2 \) and \( \bar{S} = S_1 + S_2 \) are required in the evaluation of the matrix elements of \( H_{\text{el}} \). The relationship between the two bases (10) and (12) is given by (see appendix A)

\[ \left| (\alpha_1)_{\Lambda}, (\alpha_2)_{\Lambda}, f, \Omega_f, T, m_T, P_T \right\rangle = \left| (\alpha_1)_{\Lambda}, (\alpha_2)_{\Lambda}, f, \Omega_f = \psi, T, m_T \right\rangle + P_T (-1)^{j_f - T + 1} \left| (\alpha_1)_{\Lambda}, (\alpha_2)_{\Lambda}, f, \Omega_f = -\psi, T, m_T \right\rangle, \]

and

\[ \left| (\alpha_1)_{\Lambda}, (\alpha_2)_{\Lambda}, f, \Omega_f, T, m_T \right\rangle = \left| T, m_T, \Omega_f \right\rangle \sum_{\Delta\Omega} F_{AB}^{12} \times \left\{ (\gamma_1)_{\Lambda}, (\gamma_2)_{\Lambda}, LS_{\Omega}, LS_{\phi} \right\} \left| \alpha_1, \alpha_2, \Omega_f \right\rangle. \]

The coupling coefficients \( F_{AB}^{12} \) are defined in appendix A and include the quantum numbers \( (L_1, L_2, S_1, S_2, J_1, J_2, \bar{L}, \bar{S}, \Omega_f) \) implicitly. The rotational states are

\[ \left| T, m_T, \Omega_f \right\rangle = \left\{ \frac{2 \bar{T} + 1}{4 \pi} D_{\Omega \Omega_f}^{\bar{T} m_T} (\phi, \theta, 0) \right\} \]

where \( D_{\Omega \Omega_f}^{\bar{T} m_T} (\phi, \theta, 0) \) is the Wigner rotation matrix. The analogous relationship between the states (11) and (13) follows from (15) by interchanging 1 and 2 but leaving \( A \) and \( B \) fixed.

The multichannel equation (7) require the matrix elements of \( H_{\text{rot}}, H_{\text{el}}, H_{\text{fs}} \) and \( H_{\text{fis}} \) in the basis \( \left\{ |a \rangle_{12}, |a \rangle_{21} \right\} \). The non-zero rotation terms are

\[ \langle a | \hat{T}^z | a \rangle_{12} = \langle a | \hat{T}^z | a \rangle_{21}, \]

\[ = \delta_{\phi, \phi} - \delta_{\phi, \phi} \left\{ T (T + 1) + f (f + 1) \right\} - 2 \delta_{\phi, \phi} - C_{\phi, \phi}. \]

where

\[ C_{\phi, \phi} = \begin{cases} P_T (-1)^{j_f - T + 1} K_{\tilde{\Omega} \phi} & \text{for } \phi = \phi' = \frac{1}{2}, \\ K_{\tilde{\Omega} \phi} \delta_{\phi, \phi} & \text{otherwise} \end{cases}. \]

The Coriolis coupling terms are

\[ K_{\tilde{\Omega} \phi} = |T (T + 1) - (\phi(\phi + 1) + 1) |^2, \]

and \( \rho \) denotes the set of quantum numbers \( \{ (\alpha_1)_{\Lambda}, (\alpha_2)_{\Lambda}, f, \Omega_f, T, m_T, P_T \} \).

The electronic matrix elements can be expressed in terms of the BO molecular potentials \( 2S + 1 \Lambda^e (R) \), where \( \Lambda \equiv \{ \Omega_f \} \), which are identical to that of the homonuclear \(^3\)He–\(^3\)He or \(^4\)He–\(^4\)He systems. The BO potentials are eigenvalues of \( \hat{H}_d \) for the symmetrized states:

\[ \left| \gamma_1, \gamma_2, LS_{\Omega}, LS_{\phi}, \right\rangle \left| \mu \right\rangle = N_0 \left( \left| (\gamma_1)_{\Lambda}, (\gamma_2)_{\Lambda}, LS_{\Omega}, LS_{\phi} \right\rangle \right| \left( \left| \mu \right\rangle \right) \]

\[ + (-1)^w \left( \left| (\gamma_1)_{\Lambda}, (\gamma_2)_{\Lambda}, LS_{\Omega}, LS_{\phi} \right\rangle \right| \left| \mu \right\rangle \right), \]

where \( N_0 = 1/\sqrt{2(1 + \delta_{\tau, \gamma_2})} \), \( w = 0(1) \) for gerade (ungerade) symmetry and

\[ \epsilon_{LS} = -(-1)^{L_1 + L_2 + S_1 + S_2 + S + N_0} R \frac{\rho}{P}. \]

Here \( P = \left( \epsilon_{LS} \right)^2 \) is the parity of the atomic state \( |L,m_L \rangle \) and \( N_i \) is the number of electrons on atom \( i \). Using

\[ \hat{H}_d \left| \gamma_1, \gamma_2, LS_{\Omega}, LS_{\phi}, \right\rangle \right| \left( \left| \mu \right\rangle \right) \]

\[ = \left\{ 2S + 1 \Lambda^e (R) + E_{LS} \right\} \times \left| \gamma_1, \gamma_2, LS_{\Omega}, LS_{\phi}, \right\rangle \left| \mu \right\rangle \right), \]

where \( E_{LS} \) is the asymptotic energy of the state, the matrix elements of \( \hat{H}_d \) are (see appendix A)

\[ \langle a' | \hat{H}_d | a \rangle_{12} = \delta_{\phi, \phi} \sum_{l, \Lambda} \sum_{J_1 J_2} F_{AB}^{12} T^{2T} \times \frac{1}{2} \left[ 2S + 1 \Lambda^e (R) + E_{LS} \right] \]

\[ \times 2 \left[ 2S + 1 \Lambda^e (R) - 2S + 1 \Lambda^e (R) \right], \]

where \( l' \) corresponds to the quantum numbers \( \{ l_1, l_2, \phi, \Omega_f, T, m_T, P_T \} \). The summations over \( \{ l, L \} \) disappear after the zero angular momentum of the \(^4\)He nucleus and the 1s2s \(^3\)S\(_1\) state quantum number \( L_1 = 0 \) are assigned.

We assume that the fine and hyperfine structure of the individual atoms is unaffected by the formation of the dimer.
Table 1. Fine and hyperfine structure of the \(^3\)He–\(^4\)He system. The hyperfine energies \(E_{\text{fs}}\) in MHz, of \(^3\)He for the \(2s\) \(^3\)S states are given relative to the \((j, f) = (1, 3/2)\) state and those for the \(2p\) \(^3\)P states relative to the \((j, f) = (2, 5/2)\) state. The fine structure energies \(E_s\), in MHz, of \(^4\)He for the \(2p\) \(^3\)P states are given relative to the \(j = 2\) state. The fine structure energies \(E_s\) have been shifted upwards so that the centres of gravity of the \(2s\) \(^3\)S and \(2p\) \(^3\)P manifolds are the same for \(^3\)He and \(^4\)He.

| Level | \(j\) | \(f\) | \(E_{\text{fs}}\) \(^3\)He | \(j\) | \(E_{\text{fs}}\) \(^4\)He |
|-------|-------|-------|--------------------|-------|--------------------|
| \(2p\) \(^3\)P | \(0\) | \(\frac{1}{2}\) | 343.85.941 | 0 | 319.08.83798 |
|        | \(1\) | \(\frac{1}{2}\) | 6961.104 | \(1\) | 2292.163 54 |
|        | \(1\) | \(\frac{3}{2}\) | 1780.880 | \(2\) | 4445.235 75 |
|        | \(2\) | \(\frac{3}{2}\) | 2153.072 16 | \(2\) | 2246.5671 |

so that

\[
\langle a' | \hat{H}_{\text{fs}} + \hat{H}_{\text{dfs}} | a \rangle_{12} = \delta_{a',a} \delta_{f,f} \langle \langle a_1(\alpha_1) | \hat{H}_{\text{dfs}} | \langle a_2(\alpha_2) a_3 a_4 \rangle \rangle \rangle,
\]

(25)

and

\[
21 \langle a' | \hat{H}_{\text{fs}} + \hat{H}_{\text{dfs}} | a \rangle_{21} = \delta_{a',a} \delta_{f,f} \langle \langle a_1(\alpha_1) | \hat{H}_{\text{dfs}} | \langle a_2(\alpha_2) a_3 a_4 \rangle \rangle \rangle,
\]

(26)

where \(\sigma\) denotes the set of quantum numbers \((j, \phi, T, m_T, P_\phi)\). The fine structure splittings \(\delta_{f,f}\) for the \(2p\) \(^3\)P states are the hyperfine structure matrix elements \(\langle a' | \hat{H}_{\text{dfs}} | a \rangle\) for the \(^3\)He nucleus are taken from Wu and Drake [11] and the hyperfine splitting of the \(1s2s\) \(^3\)S, \(^3\)He level from Zhao et al [12]. For the \(1s2p\) configuration of \(^3\)He there are seven relevant singlet and triplet states \(|a\rangle = |j, l, S, j, i\rangle \equiv |S, j, f\rangle\). As \(\hat{H}_{\text{dfs}}\) does not couple states with different \(f\) values, these seven states form three sets \(|0, 1, 1/2, 1, 0, 1/2, 1, 0, 1/2\rangle, \{|0, 1, 1/2, 1, 1, 1/2\}, \{|1, 0, 1, 1/2, 1, 1, 1/2\}\rangle\). The \(7 \times 7\) matrix \(\hat{A}_{\text{dfs}} \equiv \langle S, j, f \rangle \hat{H}_{\text{dfs}} | S, j, f \rangle\) is hence block diagonal with \(3 \times 3\) blocks for \(f = \frac{1}{2}\) and \(f = \frac{3}{2}\) and a single element for \(f = \frac{5}{2}\). Diagonalization of the subblocks, which include the singlet states, is necessary to obtain accurate asymptotic energies, as the coupling between singlet and triplet states shifts the energies noticeably. However, we do not want to include the ‘dressed’ singlet states (i.e. the states after diagonalization that are close to the uncoupled singlet state energies) in our multichannel basis as they are well separated in energy from the triplet states and make a negligible contribution to the scattering calculation. Fortunately, the eigenstates \(|\beta, f\rangle = \sum_{S} U_{S} |S, j, f\rangle\) resulting from the diagonalization of \(\hat{A}_{\text{dfs}}\) can be labelled in terms of approximate quantum numbers \((S, j, f)\) associated with the state \(|S, j, f\rangle\) which has the largest projection onto \(|\beta, f\rangle\), that is \(|\beta, f\rangle \equiv |S, j, f\rangle \equiv |\hat{a}\rangle\). Hence, we choose to neglect those eigenstates with predominantly singlet character \((S = 0)\), which we justify by noting that the contribution of the original singlet states \(|S = 0, j, f\rangle\) to the \(|\hat{S} = 1, j, f\rangle\) states is negligible (amplitude \(<10^{-7}\)). The final states are written explicitly as:

\[
|\hat{S}_\perp = 1, \hat{j}_\perp = f_\perp \pm \frac{1}{2}, \hat{f}_\perp \rangle = \cos(\theta_\perp) |\gamma, j = f_\perp \pm \frac{1}{2}, \hat{f}_\perp \rangle \\
\mp \sin(\theta_\perp) |\gamma, j = f_\perp \mp \frac{1}{2}, \hat{f}_\perp \rangle,
\]

(27)

for \(f_\perp = \frac{1}{2}\) and \(f_\parallel = \frac{3}{2}\), where \(\theta_\perp\) is determined from the eigenstates, and

\[
|\hat{S}_\parallel = 1, \hat{j}_\parallel = 2, f_\parallel = 5/2 \rangle = |\gamma, j = 2, f_\parallel = 5/2 \rangle.
\]

(28)

The hyperfine energies given in Table 1 define a diagonal matrix in this new basis \(|\alpha_i\rangle\) and are transformed into the \(|\alpha_i\rangle\) basis to be used in (25) for our numerical calculations.

The total matrix element \(V_\alpha(R)\) is therefore diagonal in \(T\) and \(m_T\) and its non-zero values are furthermore independent of \(m_T\).

\section{2.3. Single-channel approximation}

To make a single-channel approximation, we first neglect the Coriolis couplings in (17) to obtain sets of channels for each value of \(\phi\). We then find the adiabatic states within each of these sets by diagonalizing at each value of \(R\), the matrix

\[
V_\alpha(R) = \left\langle a' | \hat{H}_{\text{cl}} | a \right\rangle + \left\langle a' | (\hat{H}_{\text{fs}} + \hat{H}_{\text{dfs}}) | a \right\rangle + \frac{\left\langle a' | \hat{\mu}^2 | a \right\rangle_\phi}{2\mu R^2},
\]

(29)

where \(|\alpha\rangle \equiv \{|a_1, a_2 \rangle, |a_2, a_1 \rangle\rangle\) and \(\left\langle a' | \hat{\mu}^2 | a \right\rangle_\phi\) is the part of (17) with \(C_{\phi \phi}\) (i.e. the Coriolis couplings) neglected. The corresponding \(R\)-dependent eigenvectors are

\[
|\gamma\rangle = \sum_a C_{\alpha \gamma} (R) |a\rangle,
\]

(30)
where \( n = \{\phi, T, k\} \), which includes an index \( k = 0, 1, 2, \ldots \) (assigned in order of increasing energy at large \( R \)) to distinguish the different eigenvectors of the subspace \( \{\phi, T\} \), and the adiabatic potential is given by

\[
V^\text{adi}_n(R) = \sum_{\alpha, \beta} C_{\alpha, \beta}^{-1} V^\phi_\alpha C_{\alpha, \beta}.
\]

Note that the eigenvectors are degenerate in \( m_T \) and \( P_T \), which have been omitted. The radial eigenvalue equation for the rovibrational eigenstates \( |\psi_{\alpha, \gamma}\rangle = R^{-1} G_{\alpha, \gamma}(R)|n\rangle \) is then

\[
\begin{aligned}
-\frac{\hbar^2}{2\mu} \frac{d^2}{dR^2} + V^\text{adi}_n(R) - E_{\alpha, \gamma} \end{aligned} \]

\[
G_{\alpha, \gamma}(R) = 0.
\]  

We define the couplings that have been neglected in (32), which arise from \( \hat{T}_K \) and are hence proportional to the derivatives \( dC_{\alpha, \gamma}/dR \), as non-adiabatic couplings. These couplings are important only when both the diagonalization of the potential varies quickly with \( R \) and the energy difference between two adiabatic potentials is small.

We note here that there exist no special symmetries that cause couplings to disappear at particular values of \( R \). Hence, none of the adiabatic potentials within one particular set cross one another. However, it will be seen in the multichannel calculations that the non-adiabatic terms can cause diabatic transitions between these potentials, leading to effective true crossings between these adiabatic potentials.

### 2.4. Input potentials

The required BO potentials \( 1,3,5\Sigma^+,\Lambda \) and \( 1,3,5\Pi_{\lambda, u} \) were constructed as in Cocks \textit{et al} [3, 4] by matching the \textit{ab initio} short-range potentials of Deguilhem \textit{et al} [6] onto the long-range dipole-dipole plus dispersion potentials

\[
V^\text{long}_\lambda(R) = -f_{\lambda, \Lambda}(R/\lambda) C_{\lambda, \Lambda}/R^3 - C_{\Lambda, \Lambda}/R^6
\]

\[
- C_{\hat{3}, \hat{3}}/R^8 - C_{\hat{9}, \Lambda}/R^9 - C_{10, \Lambda}/R^{10},
\]

where \( f_{\lambda, \Lambda} \) is an \( R \)- and \( \Lambda \)-dependent retardation correction [13], \( \lambda = \lambda/(2\pi) = 3258.12 \alpha_0 \) where \( \lambda \) is the wavelength for the \( 2S^3S^2 \rightarrow 2p^3P \) transition and the parameters \( C_{\alpha, \lambda} \) were taken from Zhang \textit{et al} [14]. Again, motivated by our study of the \( ^4\text{He}^\rightarrow \rightarrow ^4\text{He}^\rightarrow \) system [3], we apply a \% increase to the slope of the \( 5\Sigma_{\hat{3}, \hat{3}} \) and \( 5\Pi_{\hat{3}, \hat{3}} \) potentials near their inner classical turning point. In our previous calculations, this \% increase produced excellent agreement between many of the theoretical and experimental results and brought most of the theoretical predictions to within the 20 MHz uncertainty of the experimental measurements.

The coefficients \( C_{\lambda, \Lambda} \) are of opposite sign for the \( u \) and \( g \) potentials. Consequently the dipole–dipole contribution is cancelled in the matrix elements \( 12\langle \alpha | \hat{H}_\lambda | \alpha \rangle_{12} \) and \( 21\langle \alpha | \hat{H}_\lambda | \alpha \rangle_{21} \) as expected and only contributes to the off-diagonal elements \( 21\langle \alpha | \hat{H}_\lambda | \alpha \rangle_{12} \).

### 3. Results

#### 3.1. Method

Our numerical calculations follow closely those described in [3, 4] and we briefly outline the procedure here. The numerical solution of the coupled multichannel equation (7) and each single-channel equation (32) for a single energy \( E \) is performed using the renormalized Numerov method on a grid of points consisting of connected regions with fixed step sizes. To obtain the single-channel bound states, we select only those potentials which have a minimum at long-range \( (R > 100 \alpha_0) \) and determine the bound state eigenenergies by counting the number of nodes in the wave function as a function of energy for energies less than the asymptotic energy of the single-channel, \( E_\infty = V^\text{adi}_n(\rightarrow \infty) \). The bound state energies then correspond to a change in the number of nodes (or equivalently a node at \( R \rightarrow \infty \)).

In the multichannel calculation, true bound states are unlikely to occur for energies above at least one of the channel asymptotes as couplings to open channels provide paths for dissociation. Hence, we extend our search to complex energy space \( E = E - i\Gamma \), where the value of \( \Gamma \) at a valid resonance designates the line width of the resonance. We identify these resonances by performing inward and outward integration of the equation (7) and use the inverse of the matching condition as the integrand of a contour integration. See appendix B for details.

#### 3.2. Discussion

The binding energies of the long-range states obtained using the single-channel calculation are listed in table 2. Our multichannel calculations show a large collection of resonances which appear near the asymptotic energies of the Hamiltonian. Many of these have clearly originated from bound states that lie in the short-range wells of the single-channel potentials and are not of interest in this paper. There are other resonances, which are dominated by a long-range wave function and these have been listed in tables 3 and 4. Although we have calculated the binding energies for bound levels in the adiabatic potentials for up to \( T = \frac{\pi}{2} \), we have only gone as far as \( T = \frac{\pi}{2} \) in the multichannel calculations as higher values of \( T \) introduce no significant changes in the structure of the couplings.

All of the bound levels and resonances found can be placed into three groups, depending on which asymptote they are closest to. One of these groups consists of two isolated levels only, of energy approximately 34047.8 MHz and 9202.9 MHz, which were found in the single-channel but not in the multichannel calculations. The rest of the bound levels and resonances are either close to the 4027.4 MHz, 8539.6 MHz or 8892.8 MHz asymptotes.

#### 3.2.1. Group 1: Resonances beneath the 4027.4 MHz asymptote

This asymptote corresponds to the bosonic \( ^4\text{He}^\rightarrow \) in its 2s state and the fermionic \( ^3\text{He} \) in the 2p state with \( f = \frac{3}{2} \).
and $\tilde{j} = 1$. In the single-channel calculation, a long-range well was found in the set of adiabatic potentials. However, after calculating the bound states supported by this well, we observed a strong tunneling out of the long-range well into the short-range region and so rejected these states as long-range candidates. In the multichannel calculation, however, we find relatively long-range resonances whose widths are not too large. This leads us to conclude that the adiabatic potentials must be significantly coupled by non-adiabatic terms such that the adiabatic avoided crossings between the potentials become, in the multichannel calculation, true crossings.

By revisiting these adiabatic potentials, and forcing a few non-adiabatic crossings between different potentials, we have found two additional bound levels at 3765.30 MHz and 3999.71 MHz (with binding energies of 262.07 MHz and 27.66 MHz respectively), which correspond to a pair of the multichannel resonances. Many of these resonances also have relatively small line widths.

### 3.2.2. Group 2: Resonances beneath the 8539.6 MHz and 8892.8 MHz asymptotes

For these two asymptotes, the $2p$ excitation can be found on either atom—the 8539.6 MHz asymptote corresponds to a $2s$ $^4$He atom and a $2p$ $^2$He atom with $f = \frac{1}{2}$ and $\tilde{j} = 1$, and the asymptote 8892.8 MHz corresponds to a $2s$ $^2$He with $f = \frac{1}{2}$ and a $2p$ $^4$He with $j = 2$.

To make comparisons between the single-channel and multichannel results, we have transformed the multichannel resonance wave functions into the adiabatic basis (30) and performed the integrals $\int R^{\text{asym}} \left| G_n(R) \right|^2 dR$, where $R^{\text{asym}} G_n(R)$ is the transformed wave function, in order to obtain the contribution that each adiabatic channel makes to that resonance. However, as the wave functions increase exponentially for large $R$ and are not $L^2$ normalizable, this method alone is not well defined. To obtain a useful measure of the adiabatic contributions, we fit the asymptotic shape of the function $\left| G_n(R) \right|^2$ to a form $\int R^{\text{asym}} G_n(R) = A \exp(-\text{Im}(k_n) R)$ where $\text{Im}(k_n) = \sqrt{2\nu(E - E_n^{\text{asym}})}$ and subtract an amount.

### Table 2. Single-channel rovibrational binding energies, in units of MHz, of long-range states in the $^3$He($2\ ^3S_1$)+$^4$He($2\ ^3P_j$) and $^3$He($2\ ^3P_j$)+$^4$He($2\ ^3S_1$) systems. Energies given are relative to the specified asymptotic energy $E_n^{\text{asym}}$ and the index of the adiabatic potential given by $k$.

| $\phi$ | $k$ | $E_n^{\text{asym}}$ | $\nu/T$ | $\frac{1}{2}$ | $\frac{3}{2}$ | $\frac{5}{2}$ | $\frac{7}{2}$ | $\frac{9}{2}$ |
|--------|-----|------------------|--------|-------------|-------------|-------------|-------------|-------------|
| $\frac{1}{2}$ | 13  | 8539.6           | 0      | 1311.1      | 1274.2      | 1213.0      | 1128.2      | 1020.6      |
|     |     |                  |        | 517.0       | 485.5       | 434.3       | 364.8       | 279.7       |
|     | 2   | 130.8            | 111.4  | 80.4        | 40.4        |             |             |             |
|     | 3   | 3.3              |        |             |             |             |             |             |
| $\frac{1}{2}$ | 14  | 8539.6           | 0      | 1035.8      | 1002.0      | 946.2       | 868.9       | 770.7       |
|     |     |                  |        | 325.4       | 297.7       | 252.7       | 192.0       | 117.8       |
|     | 2   | 3.7              |        |             |             |             |             |             |
| $\frac{1}{2}$ | 15  | 8892.8           | 0      | 516.6       | 478.2       | 415.3       | 330.1       | 226.6       |
|     |     |                  |        | 202.2       | 185.4       | 158.2       | 121.5       | 75.8        |
|     | 2   | 51.2             | 39.8   | 22.1        |             |             |             |             |
| $\frac{1}{2}$ | 16  | 8892.8           | 0      | 133.1       | 103.7       | 56.0        |             |             |
|     |     |                  |        |             |             |             |             |             |
| $\frac{1}{2}$ | 17  | 9207.6           | 9      | 4.6         |             |             |             |             |
|     |     |                  |        |             |             |             |             |             |
| $\frac{1}{2}$ | 22  | 34061.9         | 0      | 15.5        |             |             |             |             |
| $\frac{3}{2}$ | 10  | 8539.6           | 0      | 1313.2      | 1248.7      | 1159.5      | 1046.5      |
|     |     |                  |        | 530.9       | 475.1       | 399.2       | 305.7       |
|     | 2   | 113.0            | 79.7   | 36.7        |             |             |             |             |
| $\frac{3}{2}$ | 11  | 8892.8           | 0      | 842.7       | 782.7       | 700.0       | 596.3       |
|     |     |                  |        | 347.7       | 309.5       | 257.6       | 193.7       |
|     | 2   | 96.2             | 72.6   | 41.9        | 6.8         |             |             |             |
|     | 3   | 1.9              |        |             |             |             |             |             |
| $\frac{3}{2}$ | 12  | 8892.8           | 6      | 419.3       | 355.3       | 266.6       | 154.3       |
| $\frac{5}{2}$ | 4   | 4027.4           | 0      | 34.3        | 7.9         |             |             |             |
| $\frac{5}{2}$ | 6   | 8892.8           | 17     | 690.3       | 617.4       | 525.1       |             |             |
|     | 18  | 169.2            | 125.9  | 73.0        |             |             |             |             |
|     | 19  | 5.2              |        |             |             |             |             |             |

Note that $-\text{Im}(k_n) > 0$ always.
The results of the single-channel and multichannel analyses are shown in Table 3. The column $E_{\text{MC}}$ indicates the index of the most strongly contributing adiabatic channel to that resonance (see text) and was always found to belong to the $\phi = \frac{3}{2}$ adiabatic set. A dash indicates no particular channel had a dominant contribution. The column $E_{\text{adi}}$ gives the binding energy of a suggested assignment between the multichannel and single-channel calculations, when such an assignment is possible. The last column shows the difference in energy $\Delta E = E_{\text{MC}} - E_{\text{adi}}$ between the resonance and single-channel level.

| $T$ | $E_{\text{sc}}$ | $E_{\text{MC}}$ | $E_{\text{adi}}$ | SC Contrib | $E_{\text{adi}}$ | $\Delta E$ |
|-----|----------------|----------------|----------------|------------|----------------|---------|
| $\frac{3}{2}$ | 4027.4 | 3268.7 | 24.6 | 6 | — | — |
|     | 3791.9 | 7.3 | 7 | — | — | — |
|     | 3986.1 | 14.4 | 7 | — | — | — |
|     | 3997.4 | 0.29 | 7.8 | — | — | — |
|     | 8539.6 | 7976.5 | 31.6 | 13 | 517.0 | -45.5 |
|     | 8248.9 | 42.3 | 15 | 516.6 | -127.8 | — |
|     | 8476.3 | 12.8 | 19 | — | — | — |
|     | 8523.4 | 13.6 | 13 | 3.3 | -13.1 | — |
|     | 8892.8 | 8638.7 | 28.3 | 15 | 202.2 | -51.4 |
|     | 8651.7 | 27.7 | 15 | 202.2 | -38.4 | — |
|     | 8665.0 | 33.2 | 15 | 202.2 | -25.1 | — |
|     | 8683.6 | 38.4 | 15 | 202.2 | -6.5 | — |
|     | 8804.7 | 12.5 | 15 | 51.2 | -36.6 | — |
|     | 8872.6 | 25.4 | 16 | 133.1 | 113.9 | — |
|     | 8892.0 | 2.4 | 15 | 51.2 | 50.5 | — |
| $\frac{5}{2}$ | 4027.4 | 3268.7 | 24.6 | 6 | — | — |
|     | 3998.2 | 19.1 | 7 | — | — | — |
|     | 4013.0 | 6.6 | 8 | — | — | — |
|     | 8539.6 | 8475.5 | 13.6 | 14 | 297.7 | 232.6 |
|     | 8523.5 | 26.5 | 13 | 111.4 | 95.9 | — |
|     | 8892.8 | 8801.9 | 19.1 | 15 | 185.4 | 95.0 |
|     | 8861.7 | 22.2 | — | — | — | — |
|     | 8888.9 | 4.2 | 15 | 39.8 | 36.2 | — |
| $\frac{7}{2}$ | 4027.4 | 3268.7 | 24.6 | 6 | — | — |
|     | 3860.4 | 17.6 | 7 | — | — | — |
|     | 4006.9 | 14.7 | 8 | — | — | — |
|     | 8539.6 | 8152.6 | 20.3 | 14 | 252.7 | -135.1 |
|     | 8531.3 | 15.6 | 13 | 80.4 | 72.5 | — |
|     | 8892.8 | 8715.4 | 16.2 | 15 | 158.2 | -18.5 |
|     | 8861.0 | 13.3 | 15 | 22.1 | -9.8 | — |
|     | 8883.8 | 6.1 | 15 | 22.1 | 13.0 | — |
|     | 8888.4 | 5.4 | 15 | 22.1 | 17.6 | — |

\[ \int_{0}^{R_{\text{max}}} f_{\text{MC}}^\phi(R) dR \] from these contributions. Although this process destroys the positivity of the normalization, it provides a sufficiently clear set of relative contributions from each of the adiabatic channels. This allows us to identify the particular adiabatic channel (if it exists) that is mainly responsible for each multichannel resonance.

With these adiabatic contributions, we can make some assignments between the single-channel and multichannel results. The first note-worthy feature is that none of the $\phi = \frac{3}{2}$ or $\phi = \frac{5}{2}$ single-channel levels seem to have survived the couplings to open channels. Although these adiabatic channels do contribute, they are never dominant.

In contrast, a couple of the adiabatic potentials ($k = 15, 16$) in the $\phi = \frac{1}{2}$ set can almost entirely be identified with multichannel resonances. Although visually there is little to distinguish these adiabatic potentials from the others, we note that their minima occur at relatively small distances ($R \approx 259 a_0$ and $R \approx 276 a_0$) as opposed to the minima for the other potentials ($R \approx 300 a_0 - 400 a_0$). We also observe two clusters of resonances that appear to correspond to one single-channel level in both the $T = \frac{3}{2}$ and $T = \frac{5}{2}$ sets at binding energies of 202.2 MHz and 22.0 MHz respectively. It is not known why these clusters have appeared but they can represent an interesting regime for experiment to probe, although they suffer from relatively large line widths.

We note that the energies differ significantly between the single-channel and multichannel results and it is only with the assistance of the adiabatic contributions that we were able to make these assignments. The difference in energy $\Delta E = E_{\text{MC}} - E_{\text{adi}}$ is included in the last column of tables 3 and 4.

Although there is often a similarity between the $P_3 = +1$ and $P_3 = -1$ results, it is clear that $P_3 = -1$ has far fewer assignments to the single-channel results. In fact, the $\phi = \frac{1}{2}$ adiabatic potentials $k = 18, 19$ seem to be the origin for many of these resonances in the $P_3 = -1$ set and yet these adiabatic

| $T$ | $E_{\text{sc}}$ | $E_{\text{MC}}$ | $E_{\text{adi}}$ | SC Contrib | $E_{\text{adi}}$ | $\Delta E$ |
|-----|----------------|----------------|----------------|------------|----------------|---------|
| $\frac{3}{2}$ | 4027.4 | 3766.6 | 40.2 | 12 | — | — |
|     | 3994.2 | 4.5 | — | — | — | — |
|     | 4007.8 | 12.8 | 7.12 | — | — | — |
|     | 8539.6 | 6893.4 | 33.3 | 18 | — | — |
|     | 7951.2 | 42.2 | 19 | — | — | — |
|     | 8235.8 | 45.5 | 18 | — | — | — |
|     | 8369.3 | 49.0 | 18 | — | — | — |
|     | 8453.6 | 16.6 | 19 | — | — | — |
|     | 8532.8 | 7.3 | 13 | 3.3 | -3.7 | — |
|     | 8892.8 | 7888.3 | 16.0 | 19 | — | — |
|     | 8669.8 | 21.5 | 16 | 133.1 | 111.4 | — |
|     | 8886.2 | 3.6 | 15 | 51.2 | 44.9 | — |
| $\frac{5}{2}$ | 4027.4 | 3361.1 | 13.0 | — | — | — |
|     | 4011.9 | 2.4 | 12.7 | — | — | — |
|     | 8539.6 | 8049.1 | 24.4 | 19 | — | — |
|     | 8517.2 | 8.4 | 19 | — | — | — |
|     | 8892.8 | 8830.8 | 15.5 | 19 | — | — |
|     | 4027.4 | 3727.7 | 24.6 | 20 | — | — |
|     | 3996.0 | 0.2 | 8 | — | — | — |
|     | 4019.7 | 8.5 | 7 | — | — | — |
|     | 8539.6 | 8466.5 | 23.1 | 18 | — | — |
|     | 8513.4 | 10.4 | — | — | — | — |
|     | 8892.8 | 8715.6 | 16.6 | 15 | 158.2 | -18.3 |
|     | 8818.0 | 23.3 | 19 | — | — | — |
|     | 8883.5 | 6.5 | — | — | — | — |
|     | 8887.6 | 4.8 | 15 | 22.1 | 16.8 | — |
potentials do not support bound levels when non-adiabatic and Coriolis couplings are ignored.

3.2.3. Short-range resonances. We conclude this section with a comment about the multitude of other levels that were obtained in the multichannel calculations, but which have not been reported in this paper. These levels are easily identifiable, as they appear in a closely packed sequence of energies whose resonance wave function probabilities are reasonably uniformly distributed to all radial distances. Any visible peaks in their probabilities are concentrated at small radial distances and are usually spread over a large range of adiabatic channels.

There are two reasons why we do not discuss these resonances further. Firstly, the uncertainty in the input potentials is at its largest for short ranges and secondly, these levels will be altered by the process of Penning ionization that is likely to dramatically decrease the lifetime of these resonances when they are non-negligible for $R \leq 7 a_0$.

Although all of the long-range multi-channel levels that we identified exist only near the $E^{\infty}_3 = 4027.4$ MHz, $E^{\infty}_4 = 8539.6$ MHz and $E^{\infty}_5 = 8892.8$ MHz asymptotes, we wish to emphasize that we have scanned all asymptotes in the multichannel calculations and found no additional long-range resonances.

4. Conclusions

Long-range bound states of the excited heteronuclear $^3\text{He}^\ast–^4\text{He}^\ast$ system that dissociate to either $^3\text{He}(1s2s\ ^3S_1) + ^4\text{He}(1s2p\ ^3P)$ or $^3\text{He}(1s2p\ ^3P) + ^4\text{He}(1s2s\ ^3S_1)$, where $j = 0, 1, 2$, have been investigated using both single-channel and multichannel calculations in order to analyse the effects of Coriolis and non-adiabatic couplings.

In the single-channel calculation, several long-range wells were found in the sets of adiabatic potentials which supported a large number of bound states. In addition, the full set of coupled equations of the multichannel problem were solved by extending the calculations to allow for the identification of resonances with finite lifetimes. A large number of resonances near to the asymptotes of $4027.4$ MHz, $8539.6$ MHz and $8892.8$ MHz have been predicted and many of these could be identified with bound levels in the single-channel calculation in which non-adiabatic and Coriolis couplings were neglected.

As all of these assignments of multichannel resonances with single-channel bound levels coincided with a quantum number of $\phi = |\Omega_j| = \frac{1}{2}$, we are lead to conclude that it is important to consider the full multichannel set of equations in order to even qualitatively describe the spectroscopy of the system. This is in contrast to the homonuclear systems, in which a stronger link between single-channel and multichannel states was found. The largest discrepancy was observed for multichannel resonances of total parity $P_{\gamma} = -1$, where only a rare few resonances could be identified with single-channel levels.

There were no purely bound states identified in the calculations as all of the resonances lie above the lowest asymptote of 2153.1 MHz. However, this is not surprising due to the large number of asymptotes available to the heteronuclear configuration, allowing many opportunities for predissociation. These resonances arise from bound states of one channel being embedded in the continuum of another channel and, in that sense, are Feshbach in nature. Fortunately, some resonances do have a very small line width of less than 1 MHz near to the asymptote of 4027.4 MHz, which could prove to be very useful in photoassociation experiments.

In our previous publications that addressed the homonuclear systems of metastable helium collisions we were able to provide a set of observability criteria, which indicated a likelihood for colliding metastable atoms to be photo-associated into the resonance. Unfortunately there is not a clear and obvious choice for the preparation of a heteronuclear experimental gas mixture, so we have not included a set of observability criteria in this paper. It would be desirable, in such a case, to perform a scattering calculation similar to [15], which would consider the appropriate incoming $2s + 2s$ channels and laser coupling terms. The full scattering matrix could then be obtained, along with various cross sections relevant to experiment.

We also note that a discussion of predissociation widths due to the presence of Penning ionization is essential to make predictions for experiment. Fortunately, Penning ionization only occurs at short ranges $\leq 7 a_0$ so its impact on the long-range resonances that we have identified should be small and likely negligible.

Appendix A. Basis states and matrix elements

The body-fixed (molecular) states in the coupling scheme (9) are

$$\begin{align*}
\left( \left| \gamma_j \right| \left| \Delta f \right| \right)_A \left( \left| \gamma_j \right| \left| \delta f \right| \right)_B \left| f \right|, \left| \Omega_j \right|, \left| m, m_T \right> \\
&= \left| T, m_T, \Omega_j \right> \sum \sum \sum \sum \sum \sum \\
&\times C^{j_1j_2f_{j_3}} \Omega_{j_3} \Omega_{j_1} \Omega_{j_2} C^{j_2j_3f_{j_1}} \Omega_{j_3} \Omega_{j_1} \Omega_{j_2} C^{f_{j_3}j_3j_1} \Omega_{j_1} \Omega_{j_2} \Omega_{j_3} \\
&\times C^{j_2j_3f_{j_1}} \Omega_{j_1} \Omega_{j_2} C^{j_1j_2f_{j_3}} \Omega_{j_1} \Omega_{j_2} \Omega_{j_3} \\
&\times \left| \left| \gamma_j \right| \left| \Omega_{L_1} \Omega_{S_1} \right> \right| \left| \left| \delta f \right| \left| \Omega_{L_2} \Omega_{S_2} \right> \right>.
\end{align*}$$

(A.1)

where the transformation between the molecular and space-fixed states is, for example,

$$\begin{align*}
\left| j \Omega_j \right> &= \sum_{m,T} D^{j}_{m,\Omega_j} \left( \left| \varphi, \theta, 0 \right| \right) \left| m, m_T \right>.
\end{align*}$$

(A.2)
and $C_{i_{1}i_{2}i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma}$ is a Clebsch–Gordan coefficient.

Introducing the coupled states

$$\left|_{\gamma_{1}}\Omega_{L_{1}},\Omega_{S_{1}}\right\rangle_{A} \left|_{\gamma_{2}}\Omega_{L_{2}},\Omega_{S_{2}}\right\rangle_{B} = \sum_{\Omega_{L_{3}},\Omega_{S_{3}}} C_{i_{1}i_{2}i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} C_{i_{5}i_{6}i_{7}i_{8}}^{{\alpha_{1}\alpha_{2}}\gamma} \times \left|\gamma_{L},\gamma_{S}\right\rangle_{\Omega_{L_{1}},\Omega_{S_{1}}},$$

(A.3)

and

$$\left|\alpha_{i},\beta_{i},\Omega_{i}\right\rangle = \sum_{\Omega_{L_{i}},\Omega_{S_{i}}} C_{i_{1}i_{2}i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} \left|\alpha_{i}\Omega_{L_{i}},\beta_{i}\Omega_{S_{i}}\right\rangle,$$

(A.4)

and expressing the sums over Clebsch–Gordan coefficients in terms of Wigner 9-$j$ symbols

$$\left(\alpha_{A},\alpha_{B},\alpha_{f},\Omega_{f},T,m_{T}\right) = \left[T, m_{T}, \Omega_{f}\right] \sum_{i_{1},i_{2}} \sum_{i_{3},i_{4}} F_{i_{1}i_{2}|i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} F_{i_{3}i_{4}|i_{5}i_{6}}^{{\alpha_{1}\alpha_{2}}\gamma} \times \left|\gamma_{L},\gamma_{S}\right\rangle_{\Omega_{L_{1}},\Omega_{S_{1}}},$$

(A.5)

where $\left(\alpha_{i}\right)_{X} \equiv \left\{ \gamma_{i},\beta_{i},i_{X},f_{X}\right\}$. The coupling coefficients are defined by

$$F_{i_{1}i_{2}|i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} = \left[LS_{i_{2}|i_{3}}^{j_{1}j_{2}}\right]^{T} C_{i_{1}i_{2}i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} \left\{ L_{1} L_{2} \right\} \left\{ S_{1} S_{2} S \right\} \left\{ j_{1} j_{2} j \right\},$$

(A.6)

and

$$F_{i_{3}i_{4}|i_{5}i_{6}}^{{\alpha_{1}\alpha_{2}}\gamma} = \left[H_{i_{5}i_{6}|i_{3}i_{4}}^{j_{1}j_{2}}\right]^{T} C_{i_{3}i_{4}i_{5}i_{6}}^{{\alpha_{1}\alpha_{2}}\gamma} \left\{ j_{1} j_{2} j \right\} \left\{ i_{1} i_{2} i \right\} \left\{ f_{1} f_{2} f \right\},$$

(A.7)

where $[ab\ldots] = (2a+1)(2b+1)\ldots$. In (A.6) and (A.7) the implicit set of quantum numbers $\left(\gamma_{i},\beta_{i}\right)$ and $\left(i_{1},i_{2},j_{i},f_{i}\right)$ respectively have been suppressed.

The eigenstates of total parity $\hat{P}_{T}$ [4] are:

$$\left\langle (\alpha_{i})_{X},(\alpha_{j})_{Y},f,\Phi,T,m_{T} \right| \hat{P}_{T} \right\rangle = N_{T} \left\{ (\alpha_{i})_{X},(\alpha_{j})_{Y},f,\Phi,T,m_{T} \right\}$$

$$+ P_{T} R_{T} (-1)^{-F} \left\{ (\alpha_{i})_{X},(\alpha_{j})_{Y},f,\Phi,T,m_{T} \right\},$$

(A.8)

where $P_{T} = (-1)^{L_{T}}$ is the parity of the atomic state $|L_{T}m_{L_{T}}\rangle$, $\Phi \equiv |\Omega_{f}| = |\Omega_{T}|$ and $N_{T} = 1/\sqrt{2}$. The relationship to the $LS$ basis is completed by using (A.5).

Defining

$$F_{AB}^{\pm} = \sum_{\Omega_{1}} \left[LS_{i_{2}|i_{3}}^{j_{1}j_{2}}\right]^{T} C_{i_{1}i_{2}i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} C_{i_{5}i_{6}i_{7}i_{8}}^{{\alpha_{1}\alpha_{2}}\gamma} \times \left|\gamma_{L},\gamma_{S}\right\rangle_{\Omega_{L_{1}},\Omega_{S_{1}}},$$

(A.9)

then gives (15). The state with $1 \leftrightarrow 2$ is obtained by reordering the angular momenta to give

$$\left\langle (\alpha_{i})_{X},(\alpha_{j})_{Y},f,\Phi,T,m_{T} \right| = \left|T, m_{T}, \Omega_{f}\right\rangle \sum_{i_{1},i_{2}} \sum_{i_{3},i_{4}} F_{21}^{i_{1}i_{2}|i_{3}i_{4}}^{{\alpha_{1}\alpha_{2}}\gamma} \times \left|\gamma_{L},\gamma_{S}\right\rangle_{\Omega_{L_{1}},\Omega_{S_{1}}},$$

(A.10)

The matrix element of $\hat{H}_{d}$ in the basis (A.5) is then

$$\left\langle 12 \left(\vec{a}',\Omega'\right) = 0 \right| \hat{H}_{d} \right\rangle_{\vec{a},\Omega} = \left| 12 \left(\vec{a}',\Omega'\right) = \Phi \right| \hat{H}_{d} \right\rangle_{\vec{a},\Omega} = \left| 12 \left(\vec{a}',\Omega'\right) = \Phi \right| = 0$$

(A.11)

and, due to the Kronecker delta in $\Phi$, $\left| 12 \left(\vec{a}',\Omega'\right) = \Phi \right| \hat{H}_{d} \right\rangle_{\vec{a},\Omega} = \left| 12 \left(\vec{a}',\Omega'\right) = 0 \right| = 0.$

The same relationship is found for the 21–21 and 21–21 cases. The phase factor $(-1)^{-F}$ conveniently cancels out in the basis (A.8), due to the presence of a Kronecker delta in $T$, leaving the result:

$$\left| 12 \left(\vec{a}',\Omega'\right) = \Phi \right| \hat{H}_{d} \right\rangle_{\vec{a},\Omega} = \left| 12 \left(\vec{a}',\Omega'\right) = \Phi \right| = 0.$$

(A.12)
The same is true also for $1 \leftrightarrow 2$. The necessary matrix elements of $\hat{H}_d$ can be expressed in terms of the BO potentials for the homonuclear systems using

$$[\langle L S \rangle_{12}] \equiv \left[ \langle \gamma_1 \rangle_{A_d}, \langle \gamma_2 \rangle_{B_d}, L S \Omega_L, \Omega_S \right] = N_{\nu} \{ \nu \}, \quad (A.15)$$

and

$$[\langle L S \rangle_{21}] \equiv \left[ \langle \gamma_2 \rangle_{A_d}, \langle \gamma_1 \rangle_{B_d}, L S \Omega_L, \Omega_S \right] = N_{\nu} \{ \nu \} \{ \nu \} \{ \nu \}, \quad (A.16)$$

where we have introduced the notation

$$\nu = \{ \gamma_1, \gamma_2, L, S, \Omega_L, \Omega_S \}, \quad (A.17)$$

for the homonuclear eigenstates of gerade and ungerade symmetry. This gives

$$1 \langle \langle L S \rangle \hat{H}_d \rangle \langle L S \rangle_{12} = 2 \langle \langle L S \rangle \hat{H}_d \rangle \langle L S \rangle_{21},$$

$$= \delta_{\nu, \nu'} \frac{1}{2} \left[ 2S+1 \lambda_n^+(R) \right] + \frac{2S+1 \lambda_n^+(R) + 2 E_{\nu}^{\infty} \right]. \quad (A.18)$$

and

$$2 \langle \langle L S \rangle \hat{H}_d \rangle \langle L S \rangle_{12}$$

$$= \delta_{\nu, \nu'} \epsilon_{\nu} \epsilon_{\nu'} \frac{1}{2} \left[ 2S+1 \lambda_n^+(R) - 2S+1 \lambda_n^+(R) \right]. \quad (A.19)$$

where $\nu = \{ \gamma_1, \gamma_2, L, S, \Omega_L, \Omega_S \}$.

**Appendix B. Determination of Resonances**

To determine the position of resonances, which have the form $E = E - i \epsilon$, we choose to scan the region of complex energy space around each asymptote with a contour integral approach. For each point $E$ that is visited, we perform an inward and an outward integration of the multichannel equation (7), starting from $R = R_{\text{max}}$ and $R = R_{\text{min}}$ respectively and setting closed (open) boundary conditions for the channels below (above) the real component of $E$. These integrations end at a common point $R_\text{min}$ which allows for the definition of a matching condition $D(E) = 0$ \[3\], which is satisfied only at the location of a resonance. The integrand of the contour integral is chosen to be $f(E) = 1/D(E)$, such that the poles of $f(E)$ designate the positions of the resonances. Numerical tests have shown that $f(E)$ is analytic away from resonances and the asymptotes, which we believe is due to a nontrivial relationship to the propagator $(\hat{L} - E)^{-1}$.

Due to the analyticity of $f(E)$, we can use Cauchy’s residue theorem

$$\oint_C f(E) dE = 2\pi i \sum \text{residues}. \quad (B.1)$$

This enables a clear identification of the presence of a residue and consequently a resonance within a region of $E$-space. Using this, we may very quickly narrow the search to individual regions which tightly bound a single resonance.

For each asymptote $a$ with energy $E_a^{\infty}$, we start with a contour integration over a large box in complex $E$ space, with the real part spanning $E_a^{\infty} - 6 \delta$ to $E_a^{\infty} - 2000 \text{ MHz}$, where $\delta$ is a small parameter (we choose $\delta = 0.5 \text{ MHz}$) that avoids the non-analytic behaviour of the change in boundary conditions at the asymptote. The imaginary part of the box is chosen to span the range $\pm \delta \rightarrow -50 \text{ MHz}$, where $\delta$ is included so that true bound states do not intersect the edge of the contour. By subdividing this box, progressively narrowing the span of the real and imaginary parts, we can eliminate regions of $E$-space that contain no resonances and continue until each resonance has been identified to an accuracy of 1 MHz, after which we switch to a gradient descent method to obtain the final accuracy desired.

For each box contour integration there are four separate line integrals $L_{ij}, i = 1, 2, 3, 4$ which we perform adaptively via a Gaussian quadrature method. The final accuracy required, however, is that of the sum $S = \sum L_{ij}$ of all four integrals and this can be of the same order as the integration error itself. This is especially true for contours which contain no poles. To obtain the desired relative error in $S$, denoted by $\epsilon_S$, we perform the integration iteratively. We first obtain an estimate of the value of $S \approx S(0)$ and then, using the computed desired absolute error $\delta S(0) = \epsilon_S$, we update the desired relative error for each of the line integrals to be $\epsilon_{ij}^{(1)} = \frac{\delta S(0)}{4L_{ij}}$. Performing the line integrals again returns a new value $\delta S(1)$ which closes the iteration loop. There are two stopping conditions for this loop: (i) $\delta S/S < \epsilon_S$ which corresponds to a non-zero residue, and (ii) we reach machine precision while specifying an updated tolerance $\epsilon_{ij}^{(1)}$. The later condition corresponds to either a non-zero residue that is much smaller than the integrand (in which case we are forced to neglect it) or it corresponds to our best representation of an integration of zero. To this end, we set a small tolerance ($\epsilon_{\text{machine}} = 10^{-8}$) which is taken relative to the total value of all line integrals $\sum |L_{ij}|$ and any result $S(0) < \epsilon_{\text{machine}} \sum |L_{ij}|$ is assumed to be zero.

There is an alternative method to identify the resonances, which was used in our previous publications \[3, 4\], namely Cauchy’s argument principle which replaces the integrand of the contour integration by its logarithmic derivative. The integral is then equal to the difference in the number of zeros and poles, that is

$$\int_C f(E) dE = \frac{1}{2\pi i} \oint_C f(E) dE = n_{\text{zeros}} - n_{\text{poles}}. \quad (B.2)$$

The advantage of this method is that the integration results in integer values, allowing a clear distinction between contours

---

4 Note that this requires that no asymptote energy lies inside a contour, so that the boundary conditions do not change and the contour integrand remains analytic.

5 We note that there is the mathematical possibility for a contour to contain two resonances with residues which additively cancel, however, our tests have shown that each resonance has a distinctly different residue.

6 Note that we cache function values to avoid unnecessary repetition of calculations.
with and without a resonance. There is also no possible issue of two resonances with equal and opposite residues cancelling out. However, the disadvantage is that the method can ‘hide’ resonances when an equal number of zeros and poles lie in one region. By subdividing the region into a fine grid of box contours, we were confident that all resonances had been identified. However, with the increased number of channels in the current $^3\text{He}^*–^4\text{He}^*$ system, this becomes prohibitively expensive due to a far greater number of pairs of poles and zeros.

References

[1] Vassen W, Cohen-Tannoudji C, Leduc M, Boiron D, Westbrook C I, Truscott A, Baldwin K, Birkl G, Cancio C and Trippenbach M 2012 Rev. Mod. Phys. 84 175–210
[2] Jeltes T et al 2007 Nature 445 402–5
[3] Cocks D, Whittingham I B and Peach G 2010 J. Phys. B: At. Mol. Opt. Phys. 43 135102
[4] Cocks D, Peach G and Whittingham I B 2011 Phys. Chem. Chem. Phys. 13 18724–33
[5] Gao B 1996 Phys. Rev. A 54 2022
[6] Deguilhem B, Leininger T, Gudéa F X and Dickinson A S 2009 J. Phys. B: At. Mol. Opt. Phys. 42 015102
[7] Stas R J W, McNamara J M, Hogervorst W and Vassen W 2004 Phys. Rev. Lett. 93 053001
[8] McNamara J M, Jeltes T, Tychkov A S, Hogervorst W and Vassen W 2006 Phys. Rev. Lett. 97 080404
[9] Goosen M R, Tiecke T G, Vassen W and Kokkelmans S J M F 2010 Phys. Rev. A 82 042713
[10] Borbely J S, van Rooij R, Knoop S and Vassen W 2012 Phys. Rev. A 85 022706
[11] Wu Q and Drake G W F 2007 J. Phys. B: Atom. Mol. Opt. Phys. 40 393–402
[12] Zhao P, Lawall J R and Pipkin F M 1991 Phys. Rev. Lett. 66 592–5
[13] Meath W J 1968 J. Chem. Phys. 48 227–35
[14] Zhang J-Y, Yan Z-C, Vrinceanu D, Babb J F and Sadeghpour H R 2006 Phys. Rev. A 73 022710
[15] Cocks D and Whittingham I B 2009 Phys. Rev. A 80 023417