

# Quadrupole transitions in the bound rotational-vibrational spectrum of the hydrogen molecular ion

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**Abstract** The three-body Schrödinger equation of the  $\text{H}_2^+$  hydrogen molecular ion is solved in perimetric coordinates using the Lagrange-mesh method. Energies and wave functions of the four lowest vibrational bound or quasibound states for total orbital momenta from 0 to 40 are calculated with high accuracy. A simple calculation using the associated Gauss quadrature provides accurate quadrupole transition probabilities per time unit between those states over the whole rotational bands.

**Keywords** Hydrogen molecular ion · Transition probabilities · Lagrange-mesh method

## 1 Introduction

The  $\text{H}_2^+$  bound rotational-vibrational spectrum possesses about 420 bound states as well as about 60 narrow quasibound levels corresponding to the  $\Sigma_g$  electronic configuration and three loosely bound states corresponding to the  $\Sigma_u$  electronic configuration. For this simple three-body system, the Schrödinger equation involving Coulomb potentials can be solved with a high accuracy for both energies and wave functions.

Because of the symmetry of the two protons, electric dipole transitions are forbidden. The more complicated electric quadrupole transitions are the dominant mode of deexcitation. A systematic study of all transitions for states up to  $L = 20$  within the Born-Oppenheimer approximation has been published with two significant figures in Ref. [1]. We present accurate E2 transition probabilities without Born-Oppenheimer approximation [2]. They are obtained from three-body wave functions calculated with the Lagrange-mesh method in perimetric coordinates [3]. The Lagrange-mesh method is an approximate variational calculation using a basis of Lagrange functions and the associated Gauss quadrature [4]. It has the high accuracy of a variational approximation and the simplicity of a calculation on a mesh [5].

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## 2 Transition probabilities with Lagrange-mesh method in perimetric coordinates

For the three-body Schrödinger equation with central two-body forces, the total orbital momentum  $L$  and parity  $\pi$  are good quantum numbers. The rovibrational states in the  $\Sigma_g$  band are characterized by  $L^\pi$  and the level of excitation  $v$ , equivalent to the vibration quantum number. The parity and the proton spatial symmetry are both given by  $(-1)^L$ .

If atomic units are used, the oscillator strength for a transition with multipolarity  $\lambda$  from an initial state  $(L_i, v_i)$  with energy  $E_i$  to a final state  $(L_f, v_f)$  with energy  $E_f$  reads

$$f_{i \rightarrow f}^{(\lambda)} = \frac{(2\lambda + 1)(\lambda + 1)}{[(2\lambda + 1)!!]^2 \lambda} \alpha^{2\lambda - 2} (E_f - E_i)^{2\lambda - 1} \frac{S_{if}^{(\lambda)}}{2J_i + 1}, \quad (1)$$

where  $\alpha$  is the fine-structure constant,  $S_{if}^{(\lambda)} = |\langle L_i v_i || O^{(\lambda)} || L_f v_f \rangle|^2$  and  $O_\mu^{(\lambda)}$  is the electric multipole operator. The transition probability per time unit for  $E_f < E_i$  is given by

$$W_{i \rightarrow f}^{(\lambda)} = 2\alpha^3 (E_i - E_f)^2 f_{i \rightarrow f}^{(\lambda)}. \quad (2)$$

For  $\text{H}_2^+$ , the electric dipole operator is proportional to the electron coordinate and is therefore odd. Transitions within the  $\Sigma_g$  bands are thus forbidden.

The coordinates are expressed as three Euler angles  $\psi, \theta, \phi$  defining the orientation of the triangle formed by the three particles, and three internal coordinates  $x, y, z$  describing the shape of this triangle [6]. Each of these coordinates is the sum of two of the side lengths of the triangle minus the third one. The wave function is expanded as

$$\Psi_M^{(L^\pi)} = \sum_{K=0}^L \mathcal{D}_{MK}^{L^\pi}(\psi, \theta, \phi) \Phi_K^{(L^\pi)}(x, y, z), \quad (3)$$

where  $\mathcal{D}_{MK}^{L^\pi}(\psi, \theta, \phi)$  are normalized parity-projected Wigner functions. In practice, the sum over  $K$  can be truncated at some value  $K_{\max}$ .

The perimetric functions  $\Phi_K^{(L^\pi)}(x, y, z)$  are expanded in Lagrange functions [4, 5]

$$F_{ijk}(x, y, z) \propto \frac{L_N(x/h)}{x - hu_i} \frac{L_N(y/h)}{y - hv_j} \frac{L_{N_z}(z/h_z)}{z - h_z w_k} e^{-(x+y)/2h} e^{-z/2h_z} \quad (4)$$

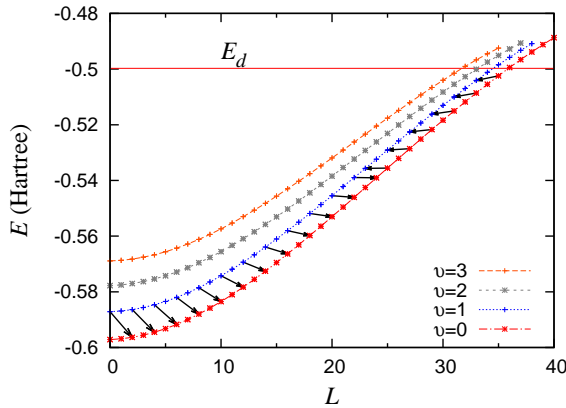
where the mesh points  $u_i, v_j, w_k$  are defined by  $L_N(u_i) = 0$ ,  $L_N(v_j) = 0$ ,  $L_{N_z}(w_k) = 0$  and  $h$  and  $h_z$  are scale parameters. Because of the symmetry of the protons, the expansion must be symmetric with respect to  $x$  and  $y$ . This basis is equivalent to a basis of products of Laguerre polynomials times the square root of the product of their weight functions. The Lagrange functions verify the Lagrange property

$$F_{ijk}(hu_{i'}, hv_{j'}, h_z w_{k'}) \propto \delta_{ii'} \delta_{jj'} \delta_{kk'}, \quad (5)$$

i.e. they vanish at all mesh points but one. Because of this property, when the consistent Gauss quadrature is used, the variational approximation of the Schrödinger equation takes the simple form of mesh equations. The potential terms are given by

$$\langle F_{ijk} | V(x, y, z) | F_{i'j'k'} \rangle \approx V(hu_i, hv_j, h_z w_k) \delta_{ii'} \delta_{jj'} \delta_{kk'}. \quad (6)$$

The potential matrix is diagonal and no integrals are required. The transition probabilities (2) are then also easily evaluated with the same Gauss quadrature.



**Fig. 1** Energy levels of calculated wave functions in the four lowest rotational bands.

**Table 1** Convergence of energies  $E_i$  and  $E_f$  and of transition probability  $W$  with respect to  $N$  and  $N_z$  for the  $(30^+, 2) \rightarrow (32^+, 0)$  transition.

$N$	$N_z$	$E_i(30^+, 2)$	$E_f(32^+, 0)$	$W$ ( $10^{-10}\text{s}^{-1}$ )
30	20	-0.508 263 395	-0.511 783 811 69	2.391 488
35	20	-0.508 263 437 6	-0.511 783 811 805 9	2.391 465 808
40	20	-0.508 263 438 21	-0.511 783 811 807 25	2.391 465 579
40	30	-0.508 263 438 21	-0.511 783 811 807 25	2.391 465 577
Ref. [7]		-0.508 263 438 18	-0.511 783 811 71	

### 3 Results

The mesh equations are solved with  $N = 40$  and  $N_z = 20$  ( $h = 0.14$ ,  $h_z = 0.4$ ) and  $K_{\max} = 2$ . The calculated states, i.e.  $v = 0 - 3$  for  $L = 0 - 40$ , are depicted in Fig. 1. The convergence of the energies and of the transition probabilities is illustrated in Table 1 for the transition between the  $(30^+, 2)$  and  $(32^+, 0)$  states. It is typical of all calculated states [2]. The accuracy on the energies reaches 13 digits for  $v = 0$  and 11 digits for  $v = 2$ . The transition probability displays a convergence at 10 digits with respect to  $N$  and  $N_z$ . However the accuracy is limited to 6-7 digits with  $K_{\max} = 2$  because of the neglect of interference terms like between  $K = 0$  and  $K' = 3$ .

Oscillator strengths are displayed in Fig. 2 for all transitions with  $L_f = L_i + 2$  between the states of Fig. 1. The oscillator strengths decrease when  $\Delta v = |v_i - v_f|$  increases. The  $\Delta v = 1$  strengths vanish near  $L = 20$  where the direction of the transition changes (see arrows in Fig. 1). They also vanish when the reduced matrix element  $S_{if}$  changes sign.

The lifetimes of the different states are displayed in Fig. 3. They are very long in the  $v = 0$  band for  $L < 15$ . The lifetime of the  $L = 2$  vibrational ground state is 3300 years. The lifetimes of the other states are comprised between 4 and 20 days.

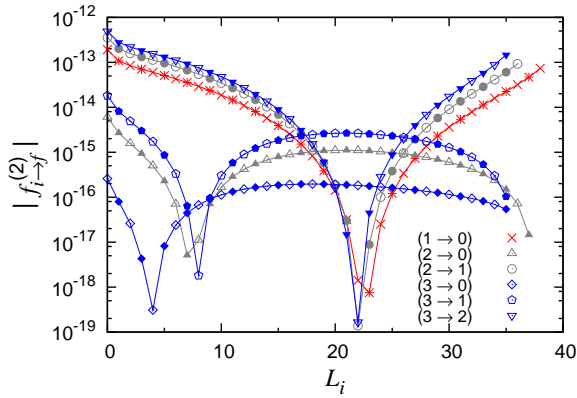


Fig. 2 Oscillator strengths relating  $L_i$  and  $L_f = L_i + 2$ .

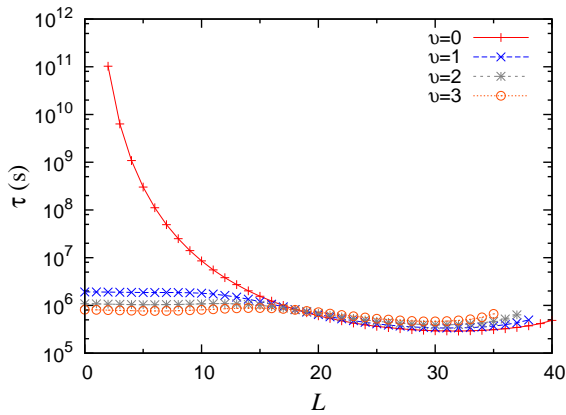


Fig. 3 Lifetimes of the states in the four lowest rotational bands.

## 4 Conclusion

The Lagrange-mesh method in perimetric coordinates does not only provide accurate energies but also accurate wave functions. With these wave functions we have determined 6-digits transition probabilities [2]. The same wave functions can be used to calculate other observables such as the static and dynamic polarizabilities of  $\text{H}_2^+$  [8].

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