

Notes on the Hamiltonian of NaCs

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I. THE HAMILTONIAN

$$\begin{bmatrix}
 H_{\text{diag}}^{X^1\Sigma} & 0 & 0 & \frac{1}{2}d_z(A \leftarrow X)E_0 & 0 & \frac{1}{2}d_{\pm 1}(B \leftarrow X)E_0 & 0 \\
 0 & H_{\text{diag}}^{c^3\Sigma} & \frac{1}{2}d_{\pm 1}(b \leftarrow a)E_0 & 0 & \frac{1}{2}d_{\pm 1}(b \leftarrow a)E_0 & 0 & \frac{1}{2}d_z(c \leftarrow a)E_0 \\
 0 & \frac{1}{2}d_{\pm 1}(b \leftarrow a)E_0 & H_{\text{diag}}^{b^3\Pi_{\pm 1}} - V_0^\Pi & \sqrt{2}\xi_1 & C_{JS} & 0 & -C_{JL} \\
 \frac{1}{2}d_z(A \leftarrow X)E_0 & 0 & \sqrt{2}\xi_1 & H_{\text{diag}}^{A^1\Sigma} & 0 & \sqrt{2}C_{JL} & 0 \\
 0 & \frac{1}{2}d_{\pm 1}(b \leftarrow a)E_0 & C_{JS} & 0 & H_{\text{diag}}^{b^3\Pi} & -\zeta_1 & \zeta_2 + C_{LS} \\
 \frac{1}{2}d_{\pm 1}(B \leftarrow X)E_0 & 0 & 0 & \sqrt{2}C_{JL} & -\zeta_1 & H_{\text{diag}}^{B^1\Pi_{\pm 1}} & \zeta_3 \\
 0 & \frac{1}{2}d_z(c \leftarrow a)E_0 & -C_{JL} & 0 & \zeta_2 + C_{LS} & \zeta_3 & H_{\text{diag}}^{c^3\Sigma}
 \end{bmatrix}$$

ξ_i - spin orbit coupling elements in the $\Omega = 0$ block

ζ_i - spin orbit coupling elements in the $\Omega = 1$ block

$$C_{JL} = -\frac{[J(J+1)]^{1/2}}{2\mu R^2}L(R)$$

$$C_{JS} = -\frac{[2J(J+1)]^{1/2}}{2\mu R^2}$$

$$C_{LS} = -\sqrt{2}\frac{L(R)}{2\mu R^2}$$

symbols and $L(R)$ defined as in Skomorowski et al. 2012 <http://arxiv.org/abs/1203.4524v2>

The terms in this 7×7 Hamiltonian are:

- In the diagonal, the term $H_{\text{diag}}^{\text{state}}$ includes the vibrational kinetic energy and the corresponding potential energy curve
- The terms on the first two row and first two columns represent the coupling due to the transition dipole moment between the singlet and triplet electronic ground states and the excited electronic states.
- The 5×5 sub-block Hamiltonian correspond to the excited states. Within this 5×5 Hamiltonian, we have the following terms:
 - The first two potentials have $\Omega = 0^+$, and their spin-orbit coupling is labelled by $\sqrt{2}\xi_1$, see the non-diagonal terms of the third square marked with the dotted line.

- The other three potentials have $\Omega = 1$, and their spin-orbit coupling is labelled by ζ_i , see the non-diagonal terms of the last square marked with the dotted line.
- In addition, the $\Omega = 0^+$ and $\Omega = 1$ electronic states are coupled through non-adiabatic Coriolis coupling. These terms are C_{JS} , $-C_{JL}$ and $\sqrt{2}C_{JL}$, whose expression are given in the 7×7 Hamiltonian shown on page 1.

I am also including the reference Wojciech Skomorowski et al, J. Chem. Phys. **136**, 194306 (2012) indicated at the bottom of the Hamiltonian, which might be also of help.

II. NUMERICAL METHOD

The mapped Fourier method transforms the time-independent Schrödinger equation associated to the Hamiltonian

$$H = T_R + V(R) \quad (1)$$

into a eigenvalue problem. So, you construct a Hamiltonian matrix of dimension $n \times n$, which has one term from the vibrational kinetic energy, represented by T_R in the Hamiltonian (1), and one part from the electronic potential curve, represented by $V(R)$ in Eq. 1. Once you diagonalize the Hamiltonian matrix, you obtain the eigenvalues and the eigenvectors, i.e., the wave functions, which are represented by vectors of dimension n .

The mapped Fourier method is used in a similar way to solve the coupled Schrödinger equation associated to the 5×5 Hamiltonian representing all the excited states. You will construct a Hamiltonian matrix but now of dimension $5n \times 5n$, having

- 5 diagonal blocks, each of dimension $n \times n$. These blocks are the Hamiltonian blocks, and are equivalent to the one you already constructed for a single electronic state Hamiltonian (1). Of course, each block is associated to a different electronic state $b^3\Pi_{\pm 1}$, $A^1\Sigma$, $b^3\Pi$, $B^1\Pi_{\pm 1}$ and $c^3\Sigma$. To construct them, just change the electronic potential curve, since the vibrational kinetic energy is the same for all of them.
- the non-diagonal blocks are due to the spin-orbit and non-adiabatic couplings. Each of these blocks also has dimension $n \times n$. Compared to the diagonal ones, they don't have the contribution from the vibrational kinetic energy, but only from the coupling terms, which are equivalent to the electronic potential curve and should be computed in a similar way.
- Note that there are non-diagonal blocks that are $n \times n$ matrices full with zeros.

Once this $5n \times 5n$ Hamiltonian matrix is diagonalized, you have all the eigenvalues and eigenvectors, and in particular you will have some vibrational states with mixing singlet and triplet character.

Note that this method could be used to solve the 7×7 Hamiltonian including the singlet and triplet electronic ground states, and once the corresponding $7n \times 7n$ Hamiltonian matrix is diagonalized, you could directly compute the FCF.

The student of Robert Moszynski has computed all the potential energy curves and the coupling terms as a function of R , I have included them on this email. I will check again with Robert if they include all the terms or not.

Concerning the dissociation limits, the X and a ground state potentials correspond to the $^2S + ^2S$ asymptote, so asymptotically they are zero. The excited state potentials should go to the nonrelativistic limit that you can get from the NIST energy levels (with the fine structure included) by using the Lande rule.