An Algorithm For Computation Of Diatomic Spectra

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Abstract. In principle, an atomic or molecular spectrum would be computed as follows: Upper and lower Hamiltonians would be enumerated in a complete basis, and numerically diagonalized to give the upper and lower energy eigenvalues and eigenvectors. The transition moments for the appropriate operator, \textit{e.g.}, the electric dipole transition moments, would be evaluated from the eigenvectors. The vacuum wavenumbers \( \tilde{\nu} \), \textit{i.e.}, energy eigenvalue differences, would be found for all non-vanishing transition moments. And the line strengths for each spectral line of wavenumber \( \tilde{\nu} \) would be determined as sum of the squares of the transition moments over all transitions producing the same \( \tilde{\nu} \). A line list that includes line strengths would be generated by repeating the above computations over the required range of upper and lower total angular momentum quantum numbers. The spectrum from \( \tilde{\nu}_{\text{min}} \) to \( \tilde{\nu}_{\text{max}} \) would be separated into a number of pixels, subsequently, the contribution of each line to each pixel is calculated using the line list. We show how this algorithm can be implemented for a diatomic spectrum if the required molecular parameters are available.

1. Introduction
This work reports our algorithm used to compute the synthetic spectra of diatomic molecules. Figure 1 shows a measured spectrum of interest in for example Laser-Induced Breakdown Spectroscopy (LIBS) \cite{1, 2, 3, 4, 5}, and it also shows two computed C\textsubscript{2} Swan spectra fitted to the experimental spectrum. With one caveat, the algorithm is the textbook method for computation of a spectrum. The caveat is that a comprehensive set of accurate diatomic parameters is required for its implementation. We describe our algorithm and give an explanation of why it is based on the Wigner-Witmer diatomic eigenfunction and not the Born-Oppenheimer approximation.

2. Computation of a diatomic spectrum
Except for the baseline corrections, the synthetic spontaneous emission spectra in Fig. (1) were computed using the following algorithm.

- For given upper total angular momentum quantum number \( J' \) and lower quantum number \( J \), the upper and lower Hamiltonian matrices \( H' \) and \( H \) are computed in the Hund’s case \( a \) basis and numerically diagonalized to obtain the eigenvalues \( F' \) and \( F \) and eigenvectors \( U' \) and \( U \),

\[
F' = U'^\dagger H' U',
\]
\[
F = U^\dagger H U.
\]
Figure 1. A recorded C\textsubscript{2} Swan spectrum [6] compared with two computed Swan spectra containing (a) a small constant and (b) a quadratic baseline. The temperature and baseline values were obtained by trial and error implemented with the Nelder-Mead extremum algorithm by varying the temperature for here a thermal distribution of excited states.

- The Hönl-London factors $S_{J',J}$ are computed [7],

$$S_{J',J} = (2J + 1) \left| \sum_{a'} \sum_{a} \langle J | a \rangle \langle a | C^{J'Ω'\Omega}_{JΩ} | a' \rangle \langle a' | J' \rangle \right|^2$$

and the term difference, i.e., line position, is computed for each non-vanishing Hönl-London factor,

$$\tilde{\nu} = F' - F \quad \text{if} \quad S_{J',J} \neq 0.$$

- A line list which includes line strengths is created by repeating the above for all required $J'$ and $J$.
- A thermal distribution of excited states and a Gaussian spectrometer slit function having a specified full-width at half-maximum (FWHM) are assumed.
- The spectrum is separated into a number of pixels, and the the contribution of each line in the computed line list to each pixel is computed.

Use of the above algorithm requires the Wigner-Witmer diatomic eigenfunction,

$$\langle r_1, r_2, \ldots, r_N, r | νvJM \rangle = \sum_{Ω=-J}^{J} \langle ρ, ζ, r_2', \ldots, r_N', r | νv \rangle D^{J*}_{Ω}\phi, θ, χ \rangle.$$  \hspace{1cm} (5)

in which the total angular momentum states are exactly separated instead of a Born-Oppenheimer eigenfunction in which segregation of electronic and nuclear coordinates is enforced thereby preventing separation of the total angular momentum. The quantum numbers in Eq. (5) are the vibrational quantum number $v$, the total angular momentum quantum number $J$, the magnetic quantum number $M$ for the $z$-component of $\mathbf{J}$, the magnetic quantum number $Ω$ for the $z'$ component of $\mathbf{J}$, and $n$ which is a symbol representing all other required quantum numbers.
and labels for continuum indices. In Eq. (5), primed and unprimed coordinates are related by coordinate rotation,

$$
\begin{bmatrix}
x' \\
y' \\
z'
\end{bmatrix} = D(\phi, \theta, \chi)
\begin{bmatrix}
x \\
y \\
z
\end{bmatrix},
$$

(6)

The Euler angles $\phi$, $\theta$, and $\chi$ and the coordinate rotation matrix $D(\phi, \theta, \chi)$ used here,

$$
D(\phi, \theta, \chi) =
\begin{bmatrix}
\cos \phi \cos \theta \cos \chi - \sin \phi \sin \chi & \sin \phi \cos \theta \cos \chi + \cos \phi \sin \chi & -\sin \theta \cos \chi \\
-\cos \phi \sin \theta & -\sin \phi \cos \theta \sin \chi - \sin \phi \cos \chi & \cos \theta \sin \chi \\
\sin \phi \sin \theta & \cos \phi \cos \theta \sin \chi - \sin \phi \cos \chi & \cos \theta
\end{bmatrix},
$$

(7)

are those used almost universally in the quantum theory of angular momentum[8, 9, 10, 11, 12, 13, 14]. Kovács[15] uses a different set of Euler angles. Primes do not appear on quantum numbers the quantum numbers are those of one of the electrons. In accord with standard practice in angular momentum theory, the polar coordinates $\rho$ (the distance of one of the electrons from the internuclear axis), $\zeta$ (this distance of this electron above or below the plane perpendicular to the internuclear axis and passing through the origin at the center of mass of the nuclei), and $r$ (the internuclear distance) because they are scalars whose value is the same in all coordinate systems. The polar coordinates $r$, $\theta$, and $\phi$ are those of the fictitious particle of reduced mass of the two nuclei who motion has replaced their motion. There are $N$ electrons and their coordinates are labeled $1, 2, \ldots, N$. The cylindrical coordinates $\rho$, $\chi$, and $\zeta$ are those of one of the electrons. In accord with standard practice in angular momentum theory, the quantum numbers $J$, $M$, and $\Omega$ refer to the total angular momentum. The spectroscopic quantum numbers $F$, $M_F$, and $\Omega_F$ replace $J$, $M$, and $\Omega$ in Eq. (5) when it is written in spectroscopic notation.

In the Wigner-Witmer diatomic eigenfunction the Euler angles $\phi$, $\theta$, and $\chi$ are both the parameters of coordinate rotation and angles of physical rotation. The diatomic molecule is perhaps the most complicated actual system in which a single set of Euler angles can serve both purposes. For example, in polyatomic theory the Euler angles $\phi$, $\theta$, and $\chi$ are physical rotations describing a frame to which the nuclei are attached, and are not the parameters of coordinate rotation $\alpha$, $\beta$, and $\gamma$ one would use to demonstrate rotational invariance and conservation of the total angular momentum in a polyatomic model which included vibrational angular momentum.

The Wigner-Eckart theorem breaks the transition moment into two parts, the so-called reduced matrix element whose value is controlled by the initial and final total angular quantum numbers and the degree of transition tensor operator, and Clebsch-Gordan coefficient whose value is controlled by the magnetic quantum numbers and the indices of the components of the tensor operator. The exact separation of the total angular momentum in the Wigner-Witmer eigenfunction simplifies and improves the accuracy of computation of the Hönl-London factors. Line positions $\nu$ and Hönl-London factors are normally independently evaluated. In the present algorithm, they are simultaneously computed. Of the myriad upper and lower term differences, only those for which the Hönl-London factor is non-vanishing become spectral lines.

The Born-Oppenheimer approximation is not totally eliminated from computation of a diatomic spectrum. It is needed to break the electronic-vibrational eigenfunction into the product of electronic and vibrational eigenfunction. The Wigner-Witmer diatomic eigenfunction exactly separates the diatomic line strength into the product of the electronic-vibrational strength $S_{n'v',nv}$ and the Hönl-London factor $S_{J',J}$,

$$
S_{n'v',J',nv,J} = S_{n'v',nv} S_{J',J},
$$

(8)

$$
S_{n'v',nv} = \left| a_0 + a_1 v' + a_2 v'^2 + \ldots \right|^2 q_{v'v}.
$$

(9)
The Born-Oppenheimer approximation separates the electronic-vibrational strength into the product of the square of the electronic transition moment,

\[ R_e(r) = a_0 + a_1 r + a_2 r^2 + \ldots, \quad (10) \]
evaluated at the \( r \)-centroids \( \bar{r}_{n v'} \),

\[ \bar{r}_{n v'} = \frac{\langle v' | r^n | v \rangle}{\langle v' | v \rangle}, \quad (11) \]
and with the Franck-Condon factors \( q_{v' v} \),

\[ q_{v' v} = \langle v' | v \rangle^2. \quad (12) \]

Whereas experimental and calculated line positions are often known with an accuracy of \( 1 : 10^6 \) or better, spectral line intensity is rarely recorded with an accuracy of better than 1%. Thus, use of the Born-Oppenheimer approximation for calculation of the electronic-vibrational strength, but not for calculation of line positions, does not introduce significant error.

3. Determination of the molecular parameters
Implementation of the algorithm described above requires a comprehensive set of accurate molecular parameters. This is not a minor proviso, and the situation is further complicated by the fact the use of the Wigner-Witmer eigenfunction modifies the manner in which diatomic parameters are determined from accurate line position measurements such as those provided by Fourier transform spectroscopy. The basic idea in both current practice [16, 17] and our determination of diatomic parameters is the calculation of matrix elements of the form

\[ \langle a_i | H_k | a_j \rangle = (n_i v_i J_i \Omega_i \Lambda_i S_i \Sigma_i | H_k | n_j v_j J_j \Omega_j \Lambda_j S_j \Sigma_j) \quad (13) \]
in which \( |a\rangle \) is a Hund’s case a basis function,

\[ |a\rangle = |n v J M \Omega \Lambda S \Sigma\rangle = \sqrt{\frac{2J + 1}{8\pi^2}} \langle \rho, \zeta, r_2', \ldots, r_N, r | n v \rangle D_{M \Omega}^{J S}(\phi, \theta, \chi) | S \Sigma \rangle \quad (14) \]
and \( H_k \) is a term from the diatomic Hamiltonian

\[ H = \sum_k H_k. \quad (15) \]

Use of the Wigner-Witmer eigenfunction breaks required matrix elements of the Hamiltonian into two parts, one the angular momentum part which can be calculated exactly and the electronic-vibrational part which, except for the very simplest molecules, cannot be calculated with spectroscopic accuracy. Use of a Born-Oppenheimer eigenfunction breaks calculation into three parts, an electronic part, a part consisting of a sum over an infinite number of Born-Oppenheimer vibrational states, and a rotational part. In general, none of the three can be done exactly. Van Vleck transformations, parity partitioning, and the concept of an “effective Hamiltonian” reduce the dimensions of the Hamiltonian matrix. We simply compute a Hamiltonian matrix composed of case a matrix elements, and let the dimension of the matrix be determined by the range of \( \Omega \) in Eq. (5) be that required make computed line positions \( \tilde{\nu}_{\text{cal}} \) equal the experimental positions \( \tilde{\nu}_{\text{exp}} \) to within the estimated accuracy of the \( \tilde{\nu}_{\text{exp}} \). With the exceptions (1) our Hamiltonian of unmodified case a matrix elements replaces the effective Hamiltonian used by others and (2) instead of using coded selection rules we use non-vanishing of the Hönl-London factor as the only selection rule, our determination of molecular parameters is identical to that described by
Trial values of upper and lower parameters are assumed, the line positions are computed, corrections to the parameters are computed from the errors in the computed line positions,
\[
\Delta \tilde{\nu} = \tilde{\nu}_{\text{cal}} - \tilde{\nu}_{\text{exp}},
\]
and the process is repeated until the corrections to the parameters become negligibly small. The algorithm for finding molecular parameters by fitting computed line positions to measured line positions is described in more detail in [19].

4. Discussion
The Wigner-Witmer paper[20] appeared about a year after the Born-Oppenheimer paper[21]. The Born and Oppenheimer work treats all molecules, but the Wigner-Witmer paper is strictly limited to the diatomic molecule. Although Born’s formulation[21, 22] in terms of
\[
\kappa = \left( \frac{m}{M_0} \right)^{1/4}
\]
in which \(m\) is the electronic mass and “where \(M_0\) can taken as any one of the nuclear masses or their mean”[22] is rarely used, the Born-Oppenheimer approximation became the foundation of molecular theory. Although the Born-Oppenheimer approximation is applicable to all molecules, in their final section Born and Oppenheimer show that the polar angle and azimuthal angle of the polar coordinates \(r, \theta, \phi\) of the internuclear vector in a diatomic molecule are exactly separable in the spherical harmonic \(Y_{\ell m}(\theta, \phi)\). The Wigner complex conjugate of the \(D\)-symbol, \(D_{m\omega}^* (\phi, \theta, \chi)\) is the mathematical extension of the spherical harmonics,
\[
Y_{\ell m}(\theta, \phi) = \sqrt{\frac{2\ell + 1}{4\pi}} D_{m0}^* (\phi, \theta, 0)
\]
which allows one to deal with the total angular momentum \(|jm\) rather that just the orbital angular momentum \(|\ell m\). The first half of the Wigner-Witmer paper is the logical extension of the Born-Oppenheimer \(Y_{\ell m}(\theta, \phi)\) result to include all three Euler angles in diatomic eigenfunction. The two-part Wigner-Witmer paper became famous for its second part which gives correlation rules relating the electronic states of a diatomic molecule to the \(L - S\) coupled states of the separated atoms. Oddly, the exact diatomic eigenfunction with which Wigner and Witmer determined their correlation rules has been ignored. About 40 years passed between publication the Wigner-Witmer paper and entry of the Wigner \(D\)-function into the literature of diatomic theory. By then, the Wigner-Witmer diatomic eigenfunction had apparently been forgotten.
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