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# Franck-Condon factors: computational approaches and recent developments

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#### Abstract

Algorithms and methodologies for the calculation of Franck-Condon integrals are reviewed. Starting from the standard approach based on the Cartesian representation of the normal modes and the use of Duschinsky's transformation and recursion formulas, methods for treating large displacements of the equilibrium positions and anharmonic and non-Condon effects are considered. Finally, posing attention to problems arising from the use of recurrence relations, some of the proposed solutions are critically reviewed evidencing new alternative approaches.

## 1 Introduction

Franck-Condon (FC) factors, *i.e.* the squares of the overlaps between the vibrational 2 wavefunctions of two electronic states, are ubiquitous in all chemico-physical processes 3 which involve transitions between electronic states: they control the shapes of elec-4 tronic absorption and emission spectra, the rates of radiationless processes, [1, 2] inter-5 nal conversions and intersystem crossings, including the whole class of redox reactions 6 (electron transfer), [3, 4, 5, 6] and electron transport through single molecules. [7, 8, 9] 7 For instance, the bandshape of an electronic transition from a manifold of thermally 8 populated vibrational states  $|\mathbf{v}\rangle$  of the ground electronic state  $|i\rangle$  to a manifold of 9 vibrational states  $|\mathbf{w}\rangle$  of an electronic excited state  $|f\rangle$  at a given temperature T can 10 be written, in Condon approximation, as:[10] 11

$$I(\omega,T) = Z^{-1} |\mu_{fi}|^2 \sum_{\mathbf{v},\mathbf{w}} e^{-\beta E(\mathbf{v})} |\langle \mathbf{w} | \mathbf{v} \rangle|^2 \delta(\omega - [E_{\mathbf{w}} - E_{\mathbf{v}} + \Delta E_{if}])$$
(1)

where Z is the vibrational partition function of the initial state,  $\Delta E_{if}$  is the electronic energy difference,  $\mu_{if}$  the electronic transition dipole moment,  $\beta = 1/k_B T$ , and  $\langle \mathbf{v} | \mathbf{w} \rangle$ is the Franck-Condon integral between the initial and final vibrational states.

Similarly, the Fermi golden rule expression for the rate of a radiationless transition between two electronic states, including also the case of electron transfer (ET) reactions, is:

$$W = \frac{2\pi}{\hbar} V^2 F(\Delta E, T), \qquad (2)$$

where V is the electronic coupling element, assumed in deriving 2 to be independent on vibrational coordinates, and  $F(\Delta E, T)$  is the Franck-Condon weighted density of states, nothing else than eq. 1 with  $\mu_{if} = 1$ .

In this paper the modern methodologies for the calculation of Franck-Condon integrals and their applications to the calculation of the shapes of vibronic spectra are reviewed. Starting from the well established approach, based on the Cartesian

representation of the normal modes, Duschinsky's normal mode transformation,[11] 24 harmonic approximation, and recurrence relations, [12, 13, 14, 15, 16, 17, 18, 19] we 25 will focus attention to the use of generalized coordinates, which can be of help in 26 the special cases of the so called floppy molecules, molecules which undergo a large 27 displacement of the equilibrium positions upon radiative transition, [20, 21, 22] and to 28 the case of large size molecules, for which the procedures making use of recurrence 29 relations pose severe limitations to the number of modes which can be excited and to 30 their maximum excitation level, discussing an alternative approach based on the gen-31 erating function method developed by Lax and Kubo, which allows not only to remove 32 any of the above limitations, but also to easily introduce the effect of the temperature, 33 thus appearing very promising for the implementation in the computational codes for 34 electronic wavefunction calculations. 35

## <sup>36</sup> 2 Duschinsky's transformation

In order to carry out the FC integral:

$$\langle \mathbf{w} | \mathbf{v} \rangle = \int d\mathbf{Q} \exp[-\tilde{\mathbf{Q}} \boldsymbol{\gamma} \mathbf{Q}/2] h_{w_1}(\sqrt{\gamma_1} Q_1) \cdots h_{w_n}(\sqrt{\gamma_n} Q_n) \times \exp[-\tilde{\mathbf{Q}}' \boldsymbol{\gamma}' \mathbf{Q}'/2] h_{v_1}(\sqrt{\gamma_1'} Q_1') \cdots h_{v_n}(\sqrt{\gamma_n'} Q_n') \quad (3)$$

<sup>37</sup> where  $\gamma$  and  $\gamma'$  are the matrices of reduced frequencies of the initial and final electronic <sup>38</sup> state respectively, the normal modes of one electronic state **Q** have to be transformed <sup>39</sup> in those of the other electronic state **Q'**. Duschinsky first recognized that normal <sup>40</sup> modes can change both directions and frequencies upon electronic transitions, and <sup>41</sup> pointed out that this could be taken into account by an affine transformation in the <sup>42</sup> space of the vibrational coordinates:[11]

$$\mathbf{Q}' = \mathbf{D}\mathbf{Q} + \mathbf{K},\tag{4}$$

<sup>43</sup> where Q' and Q are the normal modes of the two electronic states, D is a rotation
<sup>44</sup> matrix and K an equilibrium positions displacement vector.

Duschinsky's normal mode transformation must not be thought as just a mathe-45 matical mean for performing the integration, rather it is a fundamental tool for un-46 derstanding mechanistic details of both radiative and radiationless processes in poly-47 atomic molecules. It provides valuable information about modes which change their 48 vibrational quantum number during an electronic transition; those modes determine 49 the shape of the absorption bands and the dynamics of radiationless processes, since 50 the FC integrals, which in turn determine the shape of a spectral band, depend to a 51 larger extent on the displacement vector K and to a lesser extent on the component 52 of J matrix. 53

If the normal modes of the two electronic states are expressed in the Cartesian coordinate representation:

$$\boldsymbol{\xi} - \boldsymbol{\xi}_0 = \boldsymbol{\mathcal{L}} \mathbf{Q} \qquad \boldsymbol{\xi} - \boldsymbol{\xi}'_0 = \boldsymbol{\mathcal{L}}' \mathbf{Q}', \tag{5}$$

where  $\boldsymbol{\xi}_0$  and  $\boldsymbol{\xi}'_0$  are the Cartesian equilibrium nuclear coordinate vectors of the two electronic states, and  $\boldsymbol{\mathcal{L}}$  and  $\boldsymbol{\mathcal{L}}'$  are the rectangular matrices of the normal modes  $\mathbf{Q}, \mathbf{Q}'$ , then:

$$\mathbf{D} = \tilde{\boldsymbol{\mathcal{L}}}' \mathbf{T}_0 \boldsymbol{\mathcal{L}}$$
(6)

$$\mathbf{K} = \tilde{\boldsymbol{\mathcal{L}}}'(\mathbf{T}_0\boldsymbol{\xi}_0 - \boldsymbol{\xi}_0') \tag{7}$$

The  $\mathbf{T}_0$  matrix accounts for the so called zero-order axis-switching effects in the normal mode transformation, [23, 24] and is related to the sudden change of the orientation of the molecular Eckart frame upon electronic transition. In fact, Houghen has shown that the transformation between two sets of normal modes is in general non-linear and that only on condition that the reference frames of the two electronic states satisfy the same Eckart conditions it would reduce to the affine transformation proposed by Duschinsky.[24] Lucas and Ozkan derived closed formulas for fixing the nuclear coordinate reference frames of the two electronic states by introducing the so called axis switching matrix.[20, 25]

As pointed out by Houghen, axis switching effects, although generally recognized to be quite small, are however expected to be relevant in the quantitative study of rotational envelopes of the vibronic transitions: anomalous intensities can arise leading to appreciable differences between theoretical analyses without axis switching effects and experimental spectra.[24]

The  $\mathbf{T}_0$  matrix is obtained from the equilibrium geometry of the initial and final electronic states:

$$\mathbf{T}_0 = (\tilde{\mathbf{Z}}\mathbf{Z})^{1/2}\mathbf{Z}^{-1},\tag{8}$$

75 where Z is:

$$Z_{\alpha\beta} = \sum_{i} (\boldsymbol{\xi}_{0}')_{i\alpha} (\boldsymbol{\xi}_{0})_{i\beta}, \qquad \alpha, \, \beta = x, y, z.$$
(9)

<sup>76</sup> We notice that if  $\mathbf{Z}$  is symmetric  $\mathbf{T}_0$  is the identity matrix, *i.e.* if the two structures <sup>77</sup> are oriented in such a way that the resulting  $\mathbf{Z}$  matrix is symmetric then the zero <sup>78</sup> order Eckart conditions are automatically satisfied. Attention has to be payed to the <sup>79</sup> fact that there are eight solutions corresponding to the eight square roots of  $\tilde{\mathbf{Z}}\mathbf{Z}$ . The <sup>80</sup> correct solution can only be found by comparing the initial structure with that rotated <sup>81</sup> by the  $\mathbf{T}_0$  matrix.

It is worth noticing that in the above equations the reference points for the second order expansion of the initial and final electronic state potentials are their respective equilibrium structures. Such a choice is not always the best option, Domcke *et al.* have shown that in some cases it can be convenient to fix the reference point of the excited state at the equilibrium structure of the initial electronic state.[26] It is often convenient to work using dimensionless normal coordinates  $\mathbf{q}$  defined as

$$\mathbf{q} = \boldsymbol{\gamma}^{1/2} \mathbf{Q} \qquad \mathbf{q}' = \boldsymbol{\gamma}'^{1/2} \mathbf{Q}' \tag{10}$$

88 with

$$oldsymbol{\gamma} = 2\pi c oldsymbol{\omega}/\hbar \qquad oldsymbol{\gamma}' = 2\pi c oldsymbol{\omega}'/\hbar$$

where  $\omega$ ,  $\omega'$  are the diagonal matrices of the harmonic wavenumbers, and write the Duschinsky transformation as

$$\mathbf{q}' = \mathbf{J}\mathbf{q} + \mathbf{d} \tag{11}$$

91 where

$$\mathbf{J} = \boldsymbol{\gamma}^{\prime 1/2} \mathbf{D} \boldsymbol{\gamma}^{-1/2} \qquad \mathbf{d} = \boldsymbol{\gamma}^{\prime 1/2} \mathbf{K}$$
(12)

## <sup>92</sup> 3 Recurrence relations

Sharp and Rosenstock were the first to obtain an elegant expression of the Franck-Condon integral between any pair of *n*-dimensional vibrational states  $|\mathbf{v}\rangle = |v_1, ..., v_n\rangle$ and  $|\mathbf{w}\rangle = |w_1, ..., w_n\rangle$  by using the generating function of *n*-dimensional Hermite polynomials  $H_{\mathbf{v}}(\mathbf{q}) = h_{v_1}(q_1)h_{v_2}(q_2)\cdots h_{v_n}(q_n)$ :[12]

$$\exp(-\tilde{\boldsymbol{\lambda}}\boldsymbol{\lambda} + 2\tilde{\boldsymbol{\lambda}}\mathbf{q}) = \sum_{v} \frac{\lambda_{1}^{v_{1}} \cdots \lambda_{n}^{v_{n}}}{v_{1}! \cdots v_{n}!} H_{\mathbf{v}}(\mathbf{q}),$$
(13)

where  $\lambda$  is a dummy *n*-dimensional variable. From the above definition the following identities can be easily written:

$$\exp(-\tilde{\boldsymbol{\lambda}}\boldsymbol{\lambda} + 2\tilde{\boldsymbol{\lambda}}\mathbf{q} - \tilde{\mathbf{q}}\mathbf{q}/2) = \pi^{n/4} \sum_{v} \lambda_1^{v_1} \cdots \lambda_n^{v_n} \left(\frac{2^{v_1} \cdots 2^{v_n}}{v_1! \cdots v_n!}\right)^{1/2} |\mathbf{v}\rangle.$$
(14)

$$\int d\mathbf{q} \exp(-\tilde{\boldsymbol{\lambda}}\boldsymbol{\lambda} + 2\tilde{\boldsymbol{\lambda}}\mathbf{q} - \tilde{\mathbf{q}}\mathbf{q}/2 - \tilde{\boldsymbol{\rho}}\boldsymbol{\rho} + 2\tilde{\boldsymbol{\rho}}\mathbf{q}' - \tilde{\mathbf{q}}'\mathbf{q}'/2) = \pi^{n/2} \sum_{v,w} \lambda_1^{v_1} \cdots \lambda_n^{v_n} \rho^{w_1} \cdots \rho_n^{w_n} \left(\frac{2^{v_1} \cdots 2^{v_n}}{v_1! \cdots v_n!}\right)^{1/2} \left(\frac{2^{w_1} \cdots 2^{w_n}}{w_1! \cdots w_n!}\right)^{1/2} \langle \mathbf{v} | \mathbf{w} \rangle \quad (15)$$

where q, q' represent the sets of dimensionless normal coordinates of the two electronic
states, and the integration is performed over any of the two sets of coordinates (let's say
q). Using Duschinsky transformation (eq. 11) and performing the multidimensional
Gaussian integration the following master equation is obtained:

$$\exp\left\{ (\tilde{\boldsymbol{\lambda}} \ \tilde{\boldsymbol{\rho}}) \mathbf{y} - \frac{1}{2} (\tilde{\boldsymbol{\lambda}} \ \tilde{\boldsymbol{\rho}}) \mathbf{A} \begin{pmatrix} \boldsymbol{\lambda} \\ \boldsymbol{\rho} \end{pmatrix} \right\} = \frac{1}{\mathcal{N}} \sum_{v_1 \dots w_n} \frac{\lambda_1^{v_1} \dots \rho_n^{w_n}}{(v_1! \dots w_n!)^{1/2}} \langle \mathbf{v} | \mathbf{w} \rangle.$$
(16)

where the scalar  $\mathcal{N}$ , the  $2n \times 2n$  **A** matrix, and the 2*n*-dimensional **y** column vector are given by:

$$\mathcal{N} = \left[ \det \left( \mathbf{J} \mathbf{C}^{-1} \right) \right]^{1/2} \exp \left[ -\frac{1}{2} \tilde{\mathbf{d}} (\mathbf{I} - \mathbf{J} \mathbf{C}^{-1} \tilde{\mathbf{J}}/2) \mathbf{d} \right], \tag{17}$$

$$\mathbf{y} = \sqrt{2} \begin{pmatrix} -\mathbf{C}^{-1} \tilde{\mathbf{J}} \mathbf{d}/2 \\ (\mathbf{I} - \mathbf{J} \mathbf{C}^{-1} \tilde{\mathbf{J}}/2) \mathbf{d} \end{pmatrix}, \qquad \mathbf{A} = \begin{pmatrix} \mathbf{I} - \mathbf{C}^{-1} & -\mathbf{C}^{-1} \tilde{\mathbf{J}} \\ -\mathbf{J} \tilde{\mathbf{C}}^{-1} & \mathbf{I} - \mathbf{J} \mathbf{C}^{-1} \tilde{\mathbf{J}} \end{pmatrix}, \qquad (18)$$

105 with

$$\mathbf{C} = \frac{1}{2} (\mathbf{I} + \tilde{\mathbf{J}} \mathbf{J}).$$
(19)

It is immediately seen that  $\langle 0|0\rangle = \mathcal{N}$ . Recurrence relations for any FC integral can be easily obtained by taking the first order derivative with respect to a component of the  $\lambda_{\mu}$  and  $\rho_{\mu}$  vectors and equating the terms with equal powers in  $\lambda$  and  $\rho$ .[14, 16, 15] An alternative approach consists in realizing that the left-hand side of Equation 16 is nothing but the generating function of the 2*n*-dimensional adjoint Hermite polynomials  $G_{\mathbf{u}}^{\{\mathbf{R}\}}(x)$ :[27]

$$\exp\left(\tilde{\boldsymbol{\alpha}}x - \frac{1}{2}\tilde{\boldsymbol{\alpha}}\mathbf{R}\boldsymbol{\alpha}\right) = \sum_{u_1\dots u_{2n}} \frac{\alpha_1^{u_1}\dots\alpha_n^{u_{2n}}}{u_1!\dots u_{2n!}} G_{\mathbf{u}}^{\{\mathbf{R}\}}(x)$$
(20)

where  $\tilde{\alpha} = (\alpha_1, ..., \alpha_{2n})$  is a dummy variable and **R** is a symmetric  $2n \times 2n$  matrix. These polynomials satisfy the recurrence relations:[28]

$$G_{\mathbf{u}}(x) = x_k G_{\mathbf{u}-\mathbf{e}_k}(x) - \sum_{j \neq k} R_{kj} u_j G_{\mathbf{u}-\mathbf{e}_k-\mathbf{e}_j}(x) - (u_k - 1) R_{kk} G_{\mathbf{u}-2\mathbf{e}_k}(x) \qquad k = 1, .., n.$$
(21)

where  $\mathbf{e}_k$  is a vector with the k-th component unity and all the others zero. Thus the Franck-Condon integrals can be expressed in terms of a 2n-dimensional adjoint Hermite polynomials:

$$\langle \mathbf{v} | \mathbf{w} \rangle = \mathcal{N} \prod_{i} (v_i! w_i!)^{-1/2} G_{\mathbf{vw}}^{\{\mathbf{A}\}}(\mathbf{y}).$$
(22)

<sup>117</sup> Using equations 16, 22 and 21 recurrence relations can be written in a very compact <sup>118</sup> notation.[29] Indeed by using the 2*n* dimensional vector **u** to represent the sets of <sup>119</sup> vibrational quantum numbers **v** and **w** of the two electronic states, *i.e.* **u** = (**v**, **w**) <sup>120</sup> FC integrals can be written in the form a 2*n* dimensional array  $I(\mathbf{u}) = \langle \mathbf{v} | \mathbf{w} \rangle$ . Then, <sup>121</sup> letting m = 2n, we can write the recurrence relation as

$$\sqrt{u_k}I(\mathbf{u}) = y_kI(\mathbf{u} - \mathbf{e}_k) - \sum_{j}^{m} \sqrt{u_j - \delta_{kj}} A_{kj}I(\mathbf{u} - \mathbf{e}_k - \mathbf{e}_j) \qquad k = 1, ..., m$$
(23)

where the **A** matrix and the **y** vector have been previously defined, and  $\delta_{kj}$  is the Kronecker symbol. This compact formulation of FC recurrence relations can be of great help in computer implementations.

The implementation of recurrence formulas requires some attention. Indeed usually 125 one starts from the  $\langle 0|0\rangle$  integral and then goes over excited states in a well defined 126 order, choosing for each excitation step one of the 2n formulas 23. This approach can 127 be quite troublesome when a large number of vibrations are simultaneously excited. 128 Several implementations have been proposed in the literature. [30, 31, 18, 17, 19, 32] 129 Gruner and Brumer [30] have first proposed a binary-tree approach to implement the 130 recurrence relation, later exploited also by Hazra and Nooijen, [17] and by Ruhoff[32]. 131 At the moment this strategy seems to give the best results in terms of memory man-132 agement, leading however to rather complex algorithms. It is worth noticing that 133 Berkowitz' algorithm [28] for the computation of multidimensional Hermite polyno-134 mials allows to compute a polynomial of a given degree with the least number of 135 recursions. Its modification for the calculation of FC integrals is actually under inves-136 tigation. 137

#### <sup>138</sup> 3.1 Curvilinear coordinates

When the electronic transition is dominated by large equilibrium position displacements, it could be convenient to express the normal vibrations in terms of a properly chosen set of curvilinear coordinates. In that case an extension of the Duschinsky transformation is needed to compute FC integrals by using harmonic oscillator eigenfunctions.

<sup>144</sup> The quantum vibrational Hamiltonian in curvilinear coordinate is [33]:

$$\hat{H} = -\frac{\hbar^2}{2} G^{1/4} \left(\frac{\partial}{\partial \mathbf{S}}\right)^T G^{-1/2} \mathbf{G} \left(\frac{\partial}{\partial \mathbf{S}}\right) G^{1/4} + V, \qquad (24)$$

where **S** is the column vector of curvilinear internal coordinates, V is the potential energy, **G** and *G* are the metric matrix and its determinant, respectively, both depending on **S**, and the superscript *T* denotes transposition. Eq. 24 can be rewritten as:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{j,k} \frac{\partial}{\partial S_j} G_{jk}(S) \frac{\partial}{\partial S_k} + V(S) + V_{\rm kin}(S), \qquad (25)$$

where  $V_{\rm kin}$  collects the terms of the kinetic energy operator which depend only on coordinates, thus acting like a potential energy term.

The Hamiltonian in eq. 24 can be cast into a more manageable form by introducing curvilinear normal coordinates [33]. First, the so-called linearized internal coordinates, which are linear combinations of Cartesian displacements [34], are introduced:

$$\mathbf{s} = \mathbf{B}_0 \boldsymbol{\sigma},\tag{26}$$

where **s** and  $\sigma$  are the column vectors of the linearized internal and the Cartesian displacement coordinates, respectively, and **B**<sub>0</sub> is the standard Wilson **B**-matrix [34], whose elements depend only on the equilibrium geometry of the molecule.

 $\mathbf{157}$  Normal coordinates  $\mathbf{Q}$  are linear combinations of linearized internal coordinates:

$$\mathbf{s} = \mathbf{L}_0 \mathbf{Q},\tag{27}$$

158 in which:

$$\mathbf{L}_0 = \frac{\partial \mathbf{s}}{\partial \mathbf{Q}} = \mathbf{B}_0 \mathbf{M}^{-1/2} \boldsymbol{\mathcal{L}},\tag{28}$$

where **M** is the diagonal matrix of atomic masses and  $\mathcal{L}$  is the normalized matrix of normal modes in Cartesian coordinates. The linear relationship between **Q** and **s** ensures that the elements of matrix of the effective masses:

$$\mathbf{G}^0 = \mathbf{L}_0 \mathbf{L}_0^T,\tag{29}$$

 $_{162}$  do not depend on the coordinates s.

163 Then, "curvilinear normal coordinates"  $\overline{\mathbf{Q}}$ , defined as:

$$\mathbf{S} = \mathbf{L}_0 \bar{\mathbf{Q}},\tag{30}$$

are introduced so that the vibrational Hamiltonian (25) assumes the form:

$$\hat{H} = -\frac{\hbar^2}{2} \sum_{r,s} \frac{\partial}{\partial \bar{Q}_r} g_{rs}(\bar{Q}) \frac{\partial}{\partial \bar{Q}_s} + V(\bar{Q}) + V_{\rm kin}(\bar{Q}), \qquad (31)$$

165 where:

$$\mathbf{g} = \mathbf{R}^T \mathbf{G} \mathbf{R}; \quad \mathbf{R} = \left(\mathbf{L}_0^{-1}\right)^T.$$
 (32)

In the limit of infinitesimal vibrational amplitudes, curvilinear internal coordinates coincide with linearized ones and therefore (Eq.s 27 and 30) curvilinear normal coordinates also coincide with the linear ones. This in turn implies that: *i*)  $\mathbf{g}^{0}$ , i.e. the metric matrix over curvilinear normal coordinates at the zero order of expansion, coincides with the unit matrix and *ii*) anharmonic terms vanish in the potential energy expressed as a function of  $\bar{Q}$ . Therefore for finite amplitudes a power series expansion provides a kinetic energy operator of the form:

$$\hat{T} = -\frac{\hbar^2}{2} \sum_{r} \frac{\partial^2}{\partial \bar{Q}_r^2} + \Delta \hat{T} + V_{\rm kin}.$$
(33)

 $\Delta \hat{T}$  and  $V_{\rm kin}$  being the kinetic energy terms originated by the curvilinear nature of  $\bar{Q}$ :

$$\Delta \hat{T}\left(\bar{Q}, \frac{\partial}{\partial \bar{Q}}\right) = -\frac{\hbar^2}{2} \left(\sum_{r,s,t} g'_{rst} \frac{\partial}{\partial \bar{Q}_r} \bar{Q}_t \frac{\partial}{\partial \bar{Q}_s} + \frac{1}{2} \sum_{r,s,t,u} g''_{rstu} \frac{\partial}{\partial \bar{Q}_r} \bar{Q}_t \bar{Q}_u \frac{\partial}{\partial \bar{Q}_s} + \dots \right),$$
(34)

173 where:

$$g'_{rst} = \left(\frac{\partial g_{rs}}{\partial \bar{Q}_t}\right)_0 = \sum_{j,k,\ell} \left(\frac{\partial G_{jk}}{\partial S_\ell}\right)_0 R_{jr} R_{ks} L^0_{\ell t}; \quad \text{etc.}$$
(35)

<sup>174</sup> and a potential energy in the form:

$$V = 2\pi^2 c^2 \sum_r \tilde{\nu}_r^2 \bar{Q}_r^2 + \Delta V(\bar{Q})$$
(36)

where  $\Delta V$  collects the anharmonic terms of the potential and  $\tilde{\nu}_r$  are the harmonic frequencies expressed as wavenumbers. Combining Eq.s 33 and 36, the vibrational Hamiltonian can be written as:

$$\hat{H} = \hat{H}_0 + \Delta \hat{T} + \Delta V + V_{\rm kin}, \tag{37}$$

where  $\hat{H}_0$  is the harmonic Hamiltonian:

$$\hat{H}_0 = -\frac{\hbar^2}{2} \sum_r \frac{\partial}{\partial \bar{Q}_r^2} + 2\pi^2 c^2 \sum_r \tilde{\nu}_r^2 \bar{Q}_r^2, \qquad (38)$$

Eigenfunctions of  $\hat{H}$  fully accounting for anharmonicity can be obtained by means of perturbation theory [35] or variational method,[36] using the basis set of the eigenfunctions of  $\hat{H}_0$ , which allow the computation of FC integrals.

Although both  $\overline{\mathbf{Q}}$  and  $\mathbf{S}$  are curvilinear coordinates, they are linearly related (eq. 30), this is the key-point for the extension of Duschinsky's transformation in curvilinear normal coordinates.[33, 37] Reminding that internal coordinates  $\mathbf{S}$  represent displacements from equilibrium positions:

$$\mathbf{S} = \boldsymbol{\zeta} - \boldsymbol{\zeta}_0 = \mathbf{L}_0 \bar{\mathbf{Q}} \tag{39}$$

and denoting with a prime one of the electronic states involved in the transition:

$$\boldsymbol{\zeta} = \boldsymbol{\zeta}_0 + \mathbf{L}_0 \bar{\mathbf{Q}} \tag{40}$$

$$\boldsymbol{\zeta} = \boldsymbol{\zeta}_0' + \mathbf{L}_0' \bar{\mathbf{Q}}'. \tag{41}$$

By equating (40) and (41) and solving for  $\overline{\mathbf{Q}}$ :

$$\bar{\mathbf{Q}} = \mathbf{L}_0^{-1} \mathbf{L}_0' \bar{\mathbf{Q}}' + \mathbf{L}_0^{-1} \left(\boldsymbol{\zeta}_0' - \boldsymbol{\zeta}_0\right)$$
  
=  $\mathbf{J} \bar{\mathbf{Q}}' + \mathbf{K}.$  (42)

An example of results obtained by using the internal curvilinear coordinates in the
simulation of the photoelectron spectrum of ammonia is reported in fig. 1.

#### <sup>189</sup> 3.2 Perturbative approach

Although very efficient algorithms for recurrence relations have been developed, the necessity of storing a huge number of FC integrals seriously limits their application to large chemical systems.

<sup>193</sup> To overcome this difficulty Borrelli and Peluso[29] have developed a perturbative <sup>194</sup> scheme which cuts by several orders of magnitude the storage problem at the expense <sup>195</sup> of a minor loss in the accuracy of the computed integrals. The methodology starts by <sup>196</sup> considering that if no mode mixing effects occurred, **J**, **C**, and **C**<sup>-1</sup> would be diagonal <sup>197</sup> matrices, and the FC integrals could be factorized into a product of one-dimensional <sup>198</sup> overlap integrals. The **A** matrix can be partitioned as

$$\mathbf{A} = \mathbf{A}^{\circ} - \mathbf{X} \tag{43}$$

where  $\mathbf{A}^{\circ}$  is a  $2n \times 2n$  matrix consisting of four  $n \times n$  diagonal blocks:

$$\mathbf{A}^{\circ} = \begin{pmatrix} A_{11} & 0 & A_{1\ n+1} & 0 \\ 0 & \ddots & 0 & \ddots \\ A_{n+1\ 1} & 0 & A_{n+1\ n+1} & 0 \\ 0 & \ddots & 0 & \ddots \end{pmatrix}.$$
(44)

Using equation 16 and the above partitioning scheme it is possible to demonstrate that, up to the first order in the perturbing matrix  $\mathbf{X}$ , the following relation holds:

$$\langle \mathbf{v} | \mathbf{w} \rangle = \langle \mathbf{v} | \mathbf{w} \rangle^{\circ} + \mathcal{N} \sum_{r>s} \prod_{i \neq r,s} \langle v_i | w_i \rangle^{\circ} [X_{rs}^{(1)} (v_r v_s)^{1/2} \langle v_r - 1 | w_r \rangle^{\circ} \langle v_s - 1 | w_s \rangle^{\circ}$$

$$+ X_{rs}^{(2)} (w_r w_s)^{1/2} \langle v_r | w_r - 1 \rangle^{\circ} \langle v_s | w_s - 1 \rangle^{\circ}$$

$$+ 2X_{rs}^{(3)} (v_r w_s)^{1/2} \langle v_r - 1 | w_r \rangle^{\circ} \langle v_s | w_s - 1 \rangle^{\circ} ].$$
(45)

where  $\langle v_i | w_i \rangle^{\circ}$ 's are "effective" single mode FC integrals, differing somewhat from those obtained by the complete neglect of normal mode mixing, and the **X** matrix is written as

$$\mathbf{X} = \begin{pmatrix} \mathbf{X}^{(1)} & \mathbf{X}^{(3)} \\ \tilde{\mathbf{X}}^{(3)} & \mathbf{X}^{(2)} \end{pmatrix}.$$
 (46)

Equation 45 gives multi-dimensional FC integrals, with the first order corrections for normal mode mixing (see also references [38, 39]). Using the notation developed in equation 23 we can write the second order expansion in the very compact form

$$I(\mathbf{u}) = I^{\circ}(\mathbf{u}) + \sum_{r>s} \alpha_{rs} I^{\circ}(\mathbf{u} - \mathbf{e}_r - \mathbf{e}_s) + \frac{1}{2} \sum_{r>s} \sum_{p>q} \beta_{rspq} I^{\circ}(\mathbf{u} - \mathbf{e}_r - \mathbf{e}_s - \mathbf{e}_p - \mathbf{e}_q)$$
(47)

206 where

$$\alpha_{rs} = X_{rs} (u_r u_s)^{1/2} \qquad \beta_{rspq} = X_{rs} X_{pq} [u_r u_s (u_p - \delta_{rp} - \delta_{sp}) (u_q - \delta_{sq} - \delta_{rq})]^{1/2}$$
(48)

207 and  $I^{\circ}(\mathbf{u}) = \langle \mathbf{v} | \mathbf{w} \rangle^{\circ} = \prod_{i} \langle v_{i} | w_{i} \rangle^{\circ}.$ 

A closer inspection of equations 45 and 47 reveals several interesting properties. First, FC integrals between the vibronic ground state and any state with only one excited mode can be exactly computed as a product of zero order effective FC integrals. In this case the perturbation due to mode mixing vanishes to any order of the expansion. Secondly, FC integrals between states differing only for one or two quanta on mode i, and  $n_j$  quanta on mode j, with all the other quantum numbers set to zero, *i.e.*  $\langle 0 \cdots 1/2_i \cdots 0 | 0 \cdots n_j \cdots 0 \rangle$  and  $\langle 0 \cdots 0 \cdots 0 | 0 \cdots n_j \cdots 1/2_i \cdots 0 \rangle$ , can be exactly calculated by using the first order expansion. Similarly, the second order expansion gives exact results for FC integrals between states with three quanta distributed among two or three modes and any quanta on any another one, when all other modes have zero quanta, *i.e.*  $\langle 0 \cdots 2_i \cdots 1_j \cdots n_k \cdots 0 | 0 \cdots 0 \cdots 0 \rangle$ ,  $\langle 0 \cdots 0_i \cdots 1_j \cdots 0 | 0 \cdots 2_i \cdots 0_j \cdots n_k \cdots 0 \rangle$ ,  $\langle 0 \cdots 1_i \cdots 1_j \cdots 0 | 0 \cdots 1_k \cdots n_l \cdots 0 \rangle$  and similar combinations.

The perturbative method could be computationally demanding when terms higher 220 than second order are required. In such cases it can be convenient to use a different 221 partition of the A matrix. Modes which are strongly mixed upon electronic transition 222 are grouped together, so that Duschinsky's effect is treated exactly within each group. 223 In that case the  $n \ 2 \times 2 \ \mathbf{A}_i^{\circ}$ 's matrices are replaced by  $N_G$ , the number of subgroups, 224  $\mathbf{A}_i^{\circ}$ 's matrices, whose dimensions will depend on the size of each subgroup. Then, 225 by following the same procedure illustrated above, the exponential containing the  $A^{\circ}$ 226 matrix can be factorized into the product of  $N_G$  terms, each associated with one of 227 the  $\mathbf{A}_i^{\circ}$  matrices. Of course the zero order FC integral  $\langle \mathbf{v} | \mathbf{w} \rangle^{\circ}$  is no longer given 228 by a product of one-dimensional integrals over all normal coordinates, but it is now 229 factorized into a product over all groups  $N_G$  of  $g_i$ -dimensional FC integrals associated 230 with the normal coordinates of the i-th group.[29] 231

The FC integrals involving excitations of modes belonging to the same group are 232 thus exactly computed by fully accounting for mode mixing; the remaining, hopefully 233 small, Duschinsky effect is then added perturbatively at a lower order of perturbation. 234 Such an approach, denoted as mode grouping procedure, allows to attain a high accu-235 racy, speeding significantly up the calculation. Of course, the number of FC integrals 236 to be stored increases as the sizes of the  $N_G$  normal mode subsets increase. Figure 2 237 shows a comparison between exact and perturbative calculations of FC integrals in a 238 model system with five degrees of freedom. The parameters of the model are reported 239 in table 1. 240

## <sup>241</sup> 4 Strategies for large size molecules

The main problem in using equation 1 to compute a spectral bandshape is that the actual number of FC integrals to be calculated can become exceedingly large, leading to both a time consuming calculation and to memory management problems in the implementation. Algorithms based on an judicious way of choosing normal mode excitations have been developed, [40, 41, 42].

Santoro *et al.*[41] have proposed a scheme for the calculation of spectral lineshapes in which the vibronic transitions are divided into classes, each class being identified by the number of simultaneously excited modes, and the calculation of FC integrals is carried on separately for each class. In their procedure suitable restrictions to the quantum numbers of the individual modes are determined using *ad hoc* criteria, which have a semi-empirical basis. Using simple summation rules it is not too difficult to check the convergence of the calculation.

Though not mathematically rigourous such an approach can be extremely advan-254 tageous when only a few classes are needed to have a converged spectrum. However, 255 a key aspect of this procedure is that in order to avoid the storage of FC integrals, 256 after the integrals of each class have been computed they are convoluted with a line-257 shape function, thus loosing all the information about the identification of the vibronic 258 transitions. As we will discuss later, if the assignment of the vibronic peaks is not rele-259 vant, a much better solution for the calculation of lineshapes is to adopt the generating 260 function technique. 261

By using partial summation rules based on the coordinate representation of the generating function of the FC integrals, Berger *et al.*[42] were able to develop rigorous prescreening conditions which would allow to *a priori* select the most relevant set of FC integrals, which contribute to a spectral lineshape. However, their criteria do not guarantee that the calculation is indeed feasible since it could require a very large <sup>267</sup> number of FC integrals.

Although very useful, these approaches do not provide a general solution to the 268 problem of including all the important vibrational states in an electronic transition. 269 The number of these states grows in a combinatorial way as the vibrational degrees 270 of freedom and their excitation numbers increase. The storage problem could be in 271 principle overcrossed by using the direct formulation, which was originally proposed by 272 Sharp and Rosenstock for two and three simultaneously excited modes, [12] and then 273 extended and generalized by other authors, [43, 44, 45, 46, 47, 42] but the outcoming 274 equations are not of easy implementation. 275

Data storage could also be avoided if the multi-dimensional FC integrals could be factorized into a product over all normal modes of one-dimensional FC integrals, because the latter ones can be fastly computed on the occurrence, but Duschinsky's effect, *i.e.* the mixing of normal modes upon electronic transition, prevents from performing such a factorization. In the past, Duschinsky's effect has been often neglected in the calculation of FC integrals, but it can play an important role in the analysis of the fine structure of high resolution electronic spectra.[48]

The perturbative approach can speed up the calculation of individual FC integrals 283 and simplify memory management in the actual implementation of the algorithms, 284 however a procedure for the selection of vibrational states is still required. An analysis 285 of modern search algorithms is beyod the scope of this review. As far as spectroscopy 286 problems are of concern we are interested in finding all the states satisfying certaing 287 energy criteria *i.e.*, falling in a certaing energy range, and, possibly, some additional 288 constraints based on the actual values of the displacement vector  $\mathbf{y}$  and on the matrix 289 **A** of equation 16. The backtracking algorithm proposed by Kemper, Van Dijk and 290 Buck is one of the best suited for vibrational spectroscopy problems; [49] it can be 291 easily modified to take into account the above contraints, for a recent application 292 see ref. [50]). However, it is important to keep in mind that the application of the 293

<sup>294</sup> backtracking principle still requires searching in a huge state space.

From a computational point of view, the most efficient method for evaluating  $I(\omega, T)$  and  $F(\Delta E, T)$  of eq.s 1 and 2 is the generating function (GF) approach developed in the fifties by Lax and Kubo.[51, 52]

The GF approach is based on the integral representation of the delta function of eq. 1, and on the coordinate representation of the vibrational Hamiltonian operators of the initial and final states,  $\mathcal{H}_g$  and  $\mathcal{H}_e$  in 50 below. In short, the approach consists in *i*): writing  $F(\Delta E, T)$  as the inverse Fourier transform of a time correlation function  $f(\tau)$ 

$$F(\Delta E, T) = \frac{1}{2\pi} \int_{-\infty}^{+\infty} e^{i\Delta E_{eg}\tau} f(\tau) d\tau, \qquad (49)$$

303 where

$$f(\tau) = \operatorname{Tr}\{e^{-i\tau\mathcal{H}_e}e^{-(\beta-i\tau)\mathcal{H}_g}\}/\operatorname{Tr}\{e^{-\beta\mathcal{H}_g}\};\tag{50}$$

ii) modeling  $\mathcal{H}_g$  and  $\mathcal{H}_e$  in harmonic approximation, with normal modes of vibration ( $\mathbf{Q}_g$  and  $\mathbf{Q}_e$ ) differing for equilibrium positions, frequencies, and directions, and related each other by Duschinsky's transformation; iii) performing the Gaussian integration over normal modes and the trace operation which give:[51, 52]

$$f(\tau) = [\det \Phi]^{-1/2} \exp\left(-\tilde{\mathbf{K}} \mathbf{J} \mathbf{T}_g (\mathbf{T}_g + \mathbf{T}_e)^{-1} \mathbf{T}_e \tilde{\mathbf{J}} \mathbf{K}\right),$$
(51)

where

$$\mathbf{T}_{g} = \boldsymbol{\omega}_{g} \tanh[(\beta - i\tau)\boldsymbol{\omega}_{g}/2]; \qquad \mathbf{T}_{e} = \tilde{\mathbf{J}}\boldsymbol{\omega}_{e} \tanh(i\tau\boldsymbol{\omega}_{e}/2)\mathbf{J}$$
(52)

$$\mathbf{C}_{g} = \boldsymbol{\omega}_{g} / \tanh[(\beta - i\tau)\boldsymbol{\omega}_{g}/2]; \qquad \mathbf{C}_{e} = \tilde{\mathbf{J}}\boldsymbol{\omega}_{e} / \tanh(i\tau\boldsymbol{\omega}_{e}/2)\mathbf{J}$$
(53)

$$\boldsymbol{\Phi} = [2\sinh(\beta\boldsymbol{\omega}_g/2)]^{-2}\boldsymbol{\omega}_g^{-1}\sinh[(\beta-i\tau)\boldsymbol{\omega}_g](\mathbf{T}_g+\mathbf{T}_e)(\mathbf{C}_g+\mathbf{C}_e)\boldsymbol{\omega}_e^{-1}\sinh(i\tau\boldsymbol{\omega}_e),$$
(54)

 $\omega_g, \omega_e$  being the diagonal matrices of the vibrational frequencies of the initial and final states, and **J** and **K** are the rotation matrix and the displacement vector of Duschinsky's transformation, cf. eq. 42. The above formulation is very efficient for numerical treatments because the calculation of  $F(\Delta E, T)$  can be recast into a discrete Fourier transform problem

$$F(\Delta E, T) = \frac{1}{N} \sum_{k=1}^{N} w(\tau_k) f(\tau_k) e^{i\Delta E\tau_k}$$
(55)

where  $w(\tau)$  is a proper window function, necessary to avoid boundary and spectral leakage problems.[53]

The GF approach is extremely advantageous. First of all no recursion relations 315 are used, thus avoiding data storage problems. The price to pay for that is in a 316 significant lesser amount of information, because the GF formalism yields the whole 317 bandshape, without giving any information about the vibrational modes involved in 318 the electronic transition. Noteworthy, the computational cost of the GF is independent 319 of the value of the temperature used in calculation, making thus it possible the analysis 320 of the temperature dependence of the spectral bandshapes and overall of ET rates. 321 Recently the GF approach has been generalized for taking into account Herzberg-322 Teller effects. [54] A similar methodology based on a time-dependent formulation of 323 the electronic transition lineshape has been developed by Berger and Huh. 55, 56 The 324 main difference with the present formulation is that in their approach the generating 325 function is computed using the properties of coherent states. 326

## <sup>327</sup> 5 A brief list of applications

The methodologies described so far have been widely used for the interpretation of high resolution electronic spectra and radiationless processes. In particular, cavity ring down, [57, 58, 59, 60, 61] mass-threshold ionization, [62, 63, 64] photoionization, [65, 66] electron photodetachment, [67, 29] high resolution absorption, fluorescence and phosphorescence spectra [68, 69, 70, 71, 72, 73, 74, 57, 75, 76, 21, 58, 77, 59, 78, 79, 80, 81, 82, 83, 84, 85, 86, 60, 61, 87, 88, 89] as well as radiationless transition dynamics [18,  $_{334}$  90, 91, 92, 93, 6] have been successfully analysed. The case of the electron photodetachment spectrum of c-C<sub>4</sub>F<sub>8</sub> is discussed in more detail in fig. 3.

Applications to molecules exhibiting intramolecular charge transfer have been performed,[94] and those to zwitterionic species with tunable bond length alternation parameter [95] and to transient charge transfer absorption in DNA [96] are expected to give great insights in the chemico-physical properties of those species.

Finally Franck-Condon integrals have been used to study the efficiency of several ET path in the photoinduced ET in bacterial reaction centers.[97, 5, 98, 99, 100, 4, 101] Among others, pyrazine spectroscopy has been studied by using the Franck-Condon integrals to represent a fully non-adiabatic Hamiltonian. The results where in remarkable agreement with both experimental data and previous high level quantum dynamical simulations.[18, 102, 103]

Applications to floppy molecules [22, 36, 37, 104, 105] have shown the impor-346 tance of the internal coordinate representation of normal modes. In particular the 347 UV/photoelectron spectrum of ethylene and the photoelectron spectrum of ammonia 348 have attracted many researchers because very accurate computations are feasible on 349 those small size molecules, thus representing optimum test-cases for investigating the 350 quality of ab initio electronic methods, the role of Duschinsky mixing, the effect of 351 vibronic coupling and the importance of kinetic and potential anharmonicity. [13, 106, 352 65, 22, 36, 37353

Recently the FC approach has been extended to CD spectra; there the intensity of a vibronic transition from initial state i to final state f is given by the rotatory strength:

$$R_{fi}^{\text{FC}} = \text{Im} \left[ \boldsymbol{\mu}_{if}^{\text{elc},e} \cdot \boldsymbol{\mu}_{fi}^{\text{mag},e} \right] \left| \langle w_i | v_f \rangle \right|^2$$

where  $\mu^{\text{elc(mag)},e}$  is the electric(magnetic) dipole moment operator acting on electrons and  $\langle w_i | v_f \rangle$  is the FC integral. FC factors have been of great help to rationalize CD spectra; in a few cases it has been shown that only taking into account the lineshape of the transition it is possible to reproduce well resolved CD spectra in the gas phase.[107, 108]

The algorithms and methodologies described in this review have been implemented in several quantum chemical software packages. Among others MolFC and HOTFCHT have been among the first freely available software for the calculation of multidimensional FC integrals including Duschinsky effects.[109, 19]

## 366 6 Conclusions

The calculations of Franck-Condon integrals can be computationally demanding for large molecular systems. For N vibrational degrees of freedom, the number of integrals to be stored for using recurrence relations is of the order of  $O(v^N)$ , where v is the maximum quantum number on a single mode. Several techniques have been devised in order to reduce the computational complexity and the perturbative approach seems to be extremely promising.

The above techniques, however, do not solve the problem of finding the most important vibrational states which describe the vibronic envelope, which, in most cases, requires procedure not fully justified from a theoretical point of view. Searching through all the vibrational state space using a backtracking algorithm and then computing the FC integrals of the selected states is a valid alternative, but it may be possible only for medium sized molecules.

The use of FC integrals to actually compute spectral lineshapes of large molecules is seriously undermined by the combinatorial growth of the number of vibronic lines. It is worth to point out that in most cases it is much easier to use a completely different formulation of the lineshape problem based on the so-called generating function technique. [51, 52, 110, 50, 6, 111, 112] In this approach the computation of FC integrals is completely avoided, and FC calculations should only be used to assign a small number of *a posteriori* selected vibronic lines.[50, 55]

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Figure 1: The vibrational structure of the photoelectron spectrum of ammonia, the simplest molecule undergoing a large displacement of its equilibrium geometry upon photoionization. The  $\tilde{X}^2 A_1$  ionic state of ammonia has a planar equilibrium nuclear configuration, belonging to the D<sub>3h</sub> point group. In panel b) the spectrum simulated by using the Cartesian normal modes representation is reported: the bandwidth is much larger than the experimental one and progressions due to the excitation of the stretching modes, which are not present in the experimental spectrum (× symbol in panel d), appear, due to spurious displacements of the stretching coordinates yielded by Duschinsky's transformation in Cartesian coordinates. In panel c) the spectrum computed by using the rotation matrix and the displacement vector obtained in the internal linearized coordinates is reported: the spectrum agrees much better with the experimental one, but the bandwidth is smaller and the intensity in the region of longer wavenumbers rapidly decay. In panel d) the spectrum obtained with the full Hamiltonian in curvilinear coordinates, including also anharmonic potential energy terms, is reported and compared with the experimental one (×). Figure 2: Perturbative approach to the calculation of Franck-Condon factors. In panel a) the exact FC factors for the model system of table 1, consisting of five degrees of freedom, are reported. The other panels show the difference spectra obtained by subtracting to the exact FC factors those obtained by complete neglect of Duschinsky's effect (panel b), and by the first order (panel c) and second order (panel d) perturbative calculations. See ref. [29].

Figure 3: The long, 20000 cm<sup>-1</sup>, vibrational progressions observed in the electron photodetachment spectrum of c-C<sub>4</sub>F<sub>8</sub>. In the electronic ground state, c-C<sub>4</sub>F<sub>8</sub> possesses a nonplanar ring structure belonging to the D<sub>2d</sub> point group, panel a), with a double minimum potential energy surface associated with a low frequency ring-puckering vibrational coordinate, along which a facile ring inversion occurs, panel b). The effects of the two minimum energy configurations associated with the motion along the ring puckering vibration on the photoionization spectrum has been taken into account by a simple variational approach, adopting a quartic potential. The observed spectrum is reproduced with a very high accuracy, panel c), which has made the detailed assignment of all its spectral peaks possible. In the FC simulation the internal coordinate representation has been adopted; all modes have been excited, using room temperature Boltzmann population. All lines are convoluted with a Gaussian function of 25 cm<sup>-1</sup> width.

Table 1: Frequencies  $\omega$  and  $\omega'$  in cm<sup>-1</sup>, Duschinsky transformation matrix **J** and normal mode displacements **K** (Å· amu<sup>1/2</sup>) for the five mode model system.

		mode	J				K	
$\omega'$	ω		$\nu_1'$	$\nu_2'$	$ u_3'$	$\nu_4'$	$\nu_5'$	
1484	1500	$ u_1 $	0.97	0.20	0.15	-0.04	-0.05	0.507
1314	963	$\nu_2$	0.10	-0.82	-0.03	-0.13	0.00	0.210
714	668	$ u_3$	-0.02	-0.01	-1.00	0.11	-0.03	0.580
615	488	$ u_4$	-0.14	0.16	-0.13	-0.81	-0.01	0.236
370	390	$\nu_5$	0.03	0.16	-0.00	0.05	1.03	0.981