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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 wavefunctions of two electronic states, are ubiquitous in all chemico-physical processes which involve transitions between electronic states: they control the shapes of electronic absorption and emission spectra, the rates of radiationless processes,[1, 2] internal conversions and intersystem crossings, including the whole class of redox reactions (electron transfer),[3, 4, 5, 6] and electron transport through single molecules.[7, 8, 9]

For instance, the bandshape of an electronic transition from a manifold of thermally populated vibrational states $|\mathbf{v}\rangle$ of the ground electronic state $|i\rangle$ to a manifold of vibrational states $|\mathbf{w}\rangle$ of an electronic excited state $|f\rangle$ at a given temperature T can be written, in Condon approximation, as:[10]

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

where Z is the vibrational partition function of the initial state, ΔE_{if} is the electronic energy difference, μ_{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:

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

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

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

36 2 Duschinsky's transformation

In order to carry out the FC integral:

$$\begin{aligned}
 \langle \mathbf{w} | \mathbf{v} \rangle = \int d\mathbf{Q} \exp[-\tilde{\mathbf{Q}}\boldsymbol{\gamma}\mathbf{Q}/2] h_{w_1}(\sqrt{\gamma_1}Q_1) \cdots h_{w_n}(\sqrt{\gamma_n}Q_n) \times \\
 \exp[-\tilde{\mathbf{Q}}'\boldsymbol{\gamma}'\mathbf{Q}'/2] h_{v_1}(\sqrt{\gamma'_1}Q'_1) \cdots h_{v_n}(\sqrt{\gamma'_n}Q'_n) \quad (3)
 \end{aligned}$$

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

$$\mathbf{Q}' = \mathbf{D}\mathbf{Q} + \mathbf{K}, \quad (4)$$

43 where \mathbf{Q}' and \mathbf{Q} are the normal modes of the two electronic states, \mathbf{D} is a rotation
 44 matrix and \mathbf{K} an equilibrium positions displacement vector.

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

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

$$\xi - \xi_0 = \mathcal{L}\mathbf{Q} \quad \xi - \xi'_0 = \mathcal{L}'\mathbf{Q}', \quad (5)$$

56 where ξ_0 and ξ'_0 are the Cartesian equilibrium nuclear coordinate vectors of the two
 57 electronic states, and \mathcal{L} and \mathcal{L}' are the rectangular matrices of the normal modes
 58 \mathbf{Q}, \mathbf{Q}' , then:

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

$$\mathbf{K} = \tilde{\mathcal{L}}'(\mathbf{T}_0\xi_0 - \xi'_0) \quad (7)$$

59 The \mathbf{T}_0 matrix accounts for the so called zero-order axis-switching effects in the
 60 normal mode transformation,[23, 24] and is related to the sudden change of the ori-
 61 entation of the molecular Eckart frame upon electronic transition. In fact, Houghen
 62 has shown that the transformation between two sets of normal modes is in general
 63 non-linear and that only on condition that the reference frames of the two electronic

64 states satisfy the same Eckart conditions it would reduce to the affine transformation
 65 proposed by Duschinsky.[24] Lucas and Ozkan derived closed formulas for fixing the
 66 nuclear coordinate reference frames of the two electronic states by introducing the so
 67 called axis switching matrix.[20, 25]

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

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

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

75 where \mathbf{Z} is:

$$Z_{\alpha\beta} = \sum_i (\boldsymbol{\xi}'_0)_{i\alpha} (\boldsymbol{\xi}_0)_{i\beta}, \quad \alpha, \beta = x, y, z. \quad (9)$$

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

82 It is worth noticing that in the above equations the reference points for the second
 83 order expansion of the initial and final electronic state potentials are their respective
 84 equilibrium structures. Such a choice is not always the best option, Domcke *et al.*
 85 have shown that in some cases it can be convenient to fix the reference point of the
 86 excited state at the equilibrium structure of the initial electronic state.[26]

87 It is often convenient to work using dimensionless normal coordinates \mathbf{q} defined as

$$\mathbf{q} = \gamma^{1/2} \mathbf{Q} \quad \mathbf{q}' = \gamma'^{1/2} \mathbf{Q}' \quad (10)$$

88 with

$$\gamma = 2\pi c\omega/\hbar \quad \gamma' = 2\pi c\omega'/\hbar$$

89 where ω, ω' are the diagonal matrices of the harmonic wavenumbers, and write the

90 Duschinsky transformation as

$$\mathbf{q}' = \mathbf{J}\mathbf{q} + \mathbf{d} \quad (11)$$

91 where

$$\mathbf{J} = \gamma'^{1/2} \mathbf{D} \gamma^{-1/2} \quad \mathbf{d} = \gamma'^{1/2} \mathbf{K} \quad (12)$$

92 3 Recurrence relations

93 Sharp and Rosenstock were the first to obtain an elegant expression of the Franck-

94 Condon integral between any pair of n -dimensional vibrational states $|\mathbf{v}\rangle = |v_1, \dots, v_n\rangle$

95 and $|\mathbf{w}\rangle = |w_1, \dots, w_n\rangle$ by using the generating function of n -dimensional Hermite

96 polynomials $H_{\mathbf{v}}(\mathbf{q}) = h_{v_1}(q_1)h_{v_2}(q_2)\cdots h_{v_n}(q_n)$: [12]

$$\exp(-\tilde{\lambda}\boldsymbol{\lambda} + 2\tilde{\lambda}\mathbf{q}) = \sum_{\mathbf{v}} \frac{\lambda_1^{v_1} \cdots \lambda_n^{v_n}}{v_1! \cdots v_n!} H_{\mathbf{v}}(\mathbf{q}), \quad (13)$$

97 where $\boldsymbol{\lambda}$ is a dummy n -dimensional variable. From the above definition the following

98 identities can be easily written:

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

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

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

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

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

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

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

105 with

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

106 It is immediately seen that $\langle 0|0 \rangle = \mathcal{N}$. Recurrence relations for any FC integral can
107 be easily obtained by taking the first order derivative with respect to a component of
108 the λ_μ and ρ_μ vectors and equating the terms with equal powers in $\boldsymbol{\lambda}$ and $\boldsymbol{\rho}$. [14, 16, 15]

109 An alternative approach consists in realizing that the left-hand side of Equation
110 16 is nothing but the generating function of the $2n$ -dimensional adjoint Hermite poly-
111 nomials $G_{\mathbf{u}}^{\{\mathbf{R}\}}(x)$: [27]

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

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

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

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

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

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

$$\sqrt{u_k} I(\mathbf{u}) = y_k I(\mathbf{u} - \mathbf{e}_k) - \sum_j^m \sqrt{u_j - \delta_{kj}} A_{kj} I(\mathbf{u} - \mathbf{e}_k - \mathbf{e}_j) \quad k = 1, \dots, m \quad (23)$$

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

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

138 **3.1 Curvilinear coordinates**

139 When the electronic transition is dominated by large equilibrium position displace-
 140 ments, it could be convenient to express the normal vibrations in terms of a properly
 141 chosen set of curvilinear coordinates. In that case an extension of the Duschinsky
 142 transformation is needed to compute FC integrals by using harmonic oscillator eigen-
 143 functions.

144 The quantum vibrational Hamiltonian in curvilinear coordinate is [33]:

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

145 where \mathbf{S} is the column vector of curvilinear internal coordinates, V is the potential
 146 energy, \mathbf{G} and G are the metric matrix and its determinant, respectively, both de-
 147 pending on \mathbf{S} , and the superscript T denotes transposition. Eq. 24 can be rewritten
 148 as:

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

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

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

$$\mathbf{s} = \mathbf{B}_0 \boldsymbol{\sigma}, \quad (26)$$

154 where \mathbf{s} and $\boldsymbol{\sigma}$ are the column vectors of the linearized internal and the Cartesian
 155 displacement coordinates, respectively, and \mathbf{B}_0 is the standard Wilson \mathbf{B} -matrix [34],
 156 whose elements depend only on the equilibrium geometry of the molecule.

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

$$\mathbf{s} = \mathbf{L}_0 \mathbf{Q}, \quad (27)$$

158 in which:

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

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

$$\mathbf{G}^0 = \mathbf{L}_0 \mathbf{L}_0^T, \quad (29)$$

162 do not depend on the coordinates \mathbf{s} .

163 Then, “curvilinear normal coordinates” $\bar{\mathbf{Q}}$, defined as:

$$\mathbf{S} = \mathbf{L}_0 \bar{\mathbf{Q}}, \quad (30)$$

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

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

165 where:

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

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

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

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

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

173 where:

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

174 and a potential energy in the form:

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

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

$$\hat{H} = \hat{H}_0 + \Delta\hat{T} + \Delta V + V_{\text{kin}}, \quad (37)$$

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

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

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

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

$$\mathbf{S} = \boldsymbol{\zeta} - \boldsymbol{\zeta}_0 = \mathbf{L}_0 \bar{\mathbf{Q}} \quad (39)$$

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

$$\zeta = \zeta_0 + \mathbf{L}_0 \bar{\mathbf{Q}} \quad (40)$$

$$\zeta = \zeta'_0 + \mathbf{L}'_0 \bar{\mathbf{Q}}'. \quad (41)$$

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

$$\begin{aligned} \bar{\mathbf{Q}} &= \mathbf{L}_0^{-1} \mathbf{L}'_0 \bar{\mathbf{Q}}' + \mathbf{L}_0^{-1} (\zeta'_0 - \zeta_0) \\ &= \mathbf{J} \bar{\mathbf{Q}}' + \mathbf{K}. \end{aligned} \quad (42)$$

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

189 **3.2 Perturbative approach**

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

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

$$\mathbf{A} = \mathbf{A}^\circ - \mathbf{X} \quad (43)$$

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

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

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:

$$\begin{aligned} \langle \mathbf{v} | \mathbf{w} \rangle &= \langle \mathbf{v} | \mathbf{w} \rangle^\circ + \mathcal{N} \sum_{r>s} \prod_{i \neq r,s} \langle v_i | w_i \rangle^\circ [X_{rs}^{(1)} (v_r v_s)^{1/2} \langle v_r - 1 | w_r \rangle^\circ \langle v_s - 1 | w_s \rangle^\circ \\ &\quad + X_{rs}^{(2)} (w_r w_s)^{1/2} \langle v_r | w_r - 1 \rangle^\circ \langle v_s | w_s - 1 \rangle^\circ \\ &\quad + 2X_{rs}^{(3)} (v_r w_s)^{1/2} \langle v_r - 1 | w_r \rangle^\circ \langle v_s | w_s - 1 \rangle^\circ]. \end{aligned} \quad (45)$$

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

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

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

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

206 where

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

207 and $I^\circ(\mathbf{u}) = \langle \mathbf{v} | \mathbf{w} \rangle^\circ = \prod_i \langle v_i | w_i \rangle^\circ$.

208 A closer inspection of equations 45 and 47 reveals several interesting properties.
 209 First, FC integrals between the vibronic ground state and any state with only one
 210 excited mode can be exactly computed as a product of zero order effective FC inte-
 211 grals. In this case the perturbation due to mode mixing vanishes to any order of the
 212 expansion. Secondly, FC integrals between states differing only for one or two quanta
 213 on mode i , and n_j quanta on mode j , with all the other quantum numbers set to zero,

214 *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
 215 calculated by using the first order expansion. Similarly, the second order expansion
 216 gives exact results for FC integrals between states with three quanta distributed among
 217 two or three modes and any quanta on any another one, when all other modes have zero
 218 quanta, *i.e.* $\langle 0 \cdots 2_i \cdots 1_j \cdots n_k \cdots 0 | 0 \cdots 0 \cdots 0 \rangle$, $\langle 0 \cdots 0_i \cdots 1_j \cdots 0 | 0 \cdots 2_i \cdots 0_j \cdots n_k \cdots 0 \rangle$,
 219 $\langle 0 \cdots 1_i \cdots 1_j \cdots 0 | 0 \cdots 1_k \cdots n_l \cdots 0 \rangle$ and similar combinations.

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

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

241 4 Strategies for large size molecules

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

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

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

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

267 number of FC integrals.

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

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

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

294 backtracking principle still requires searching in a huge state space.

295 From a computational point of view, the most efficient method for evaluating
 296 $I(\omega, T)$ and $F(\Delta E, T)$ of eq.s 1 and 2 is the generating function (GF) approach devel-
 297 oped in the fifties by Lax and Kubo.[51, 52]

298 The GF approach is based on the integral representation of the delta function of
 299 eq. 1, and on the coordinate representation of the vibrational Hamiltonian operators
 300 of the initial and final states, \mathcal{H}_g and \mathcal{H}_e in 50 below. In short, the approach consists
 301 in *i)*: writing $F(\Delta E, T)$ as the inverse Fourier transform of a time correlation function
 302 $f(\tau)$

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

303 where

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

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

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

where

$$\mathbf{T}_g = \boldsymbol{\omega}_g \tanh[(\beta - i\tau)\boldsymbol{\omega}_g/2]; \quad \mathbf{T}_e = \tilde{\mathbf{J}}\boldsymbol{\omega}_e \tanh(i\tau\boldsymbol{\omega}_e/2)\mathbf{J} \quad (52)$$

$$\mathbf{C}_g = \boldsymbol{\omega}_g / \tanh[(\beta - i\tau)\boldsymbol{\omega}_g/2]; \quad \mathbf{C}_e = \tilde{\mathbf{J}}\boldsymbol{\omega}_e / \tanh(i\tau\boldsymbol{\omega}_e/2)\mathbf{J} \quad (53)$$

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

308 $\boldsymbol{\omega}_g, \boldsymbol{\omega}_e$ being the diagonal matrices of the vibrational frequencies of the initial and
 309 final states, and \mathbf{J} and \mathbf{K} are the rotation matrix and the displacement vector of
 310 Duschinsky's transformation, cf. eq. 42.

311 The above formulation is very efficient for numerical treatments because the cal-
312 culation of $F(\Delta E, T)$ can be recast into a discrete Fourier transform problem

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

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

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

327 5 A brief list of applications

328 The methodologies described so far have been widely used for the interpretation of
329 high resolution electronic spectra and radiationless processes. In particular, cavity ring
330 down,[57, 58, 59, 60, 61] mass-threshold ionization,[62, 63, 64] photoionization,[65, 66]
331 electron photodetachment,[67, 29] high resolution absorption, fluorescence and phos-
332 phorescence spectra[68, 69, 70, 71, 72, 73, 74, 57, 75, 76, 21, 58, 77, 59, 78, 79, 80, 81,
333 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 photode-
335 tachment spectrum of $c\text{-C}_4\text{F}_8$ is discussed in more detail in fig. 3.

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

340 Finally Franck-Condon integrals have been used to study the efficiency of several
341 ET path in the photoinduced ET in bacterial reaction centers.[97, 5, 98, 99, 100, 4, 101]

342 Among others, pyrazine spectroscopy has been studied by using the Franck-Condon
343 integrals to represent a fully non-adiabatic Hamiltonian. The results where in re-
344 markable agreement with both experimental data and previous high level quantum
345 dynamical simulations.[18, 102, 103]

346 Applications to floppy molecules[22, 36, 37, 104, 105] have shown the impor-
347 tance of the internal coordinate representation of normal modes. In particular the
348 UV/photoelectron spectrum of ethylene and the photoelectron spectrum of ammonia
349 have attracted many researchers because very accurate computations are feasible on
350 those small size molecules, thus representing optimum test-cases for investigating the
351 quality of ab initio electronic methods, the role of Duschinsky mixing, the effect of
352 vibronic coupling and the importance of kinetic and potential anharmonicity.[13, 106,
353 65, 22, 36, 37]

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

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

357 where $\boldsymbol{\mu}^{\text{elc(mag)},e}$ is the electric(magnetic) dipole moment operator acting on electrons
358 and $\langle w_i | v_f \rangle$ is the FC integral. FC factors have been of great help to rationalize

359 CD spectra; in a few cases it has been shown that only taking into account the line-
360 shape of the transition it is possible to reproduce well resolved CD spectra in the gas
361 phase.[107, 108]

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

366 6 Conclusions

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

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

379 The use of FC integrals to actually compute spectral lineshapes of large molecules
380 is seriously undermined by the combinatorial growth of the number of vibronic lines.
381 It is worth to point out that in most cases it is much easier to use a completely differ-
382 ent formulation of the lineshape problem based on the so-called generating function
383 technique. [51, 52, 110, 50, 6, 111, 112] In this approach the computation of FC inte-

384 grals is completely avoided, and FC calculations should only be used to assign a small
385 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}^2A_1 ionic state of ammonia has a planar equilibrium nuclear configuration, belonging to the D_{3h} 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 (\times 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 (\times).

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^{-1} , vibrational progressions observed in the electron photodetachment spectrum of $c\text{-C}_4\text{F}_8$. In the electronic ground state, $c\text{-C}_4\text{F}_8$ possesses a nonplanar ring structure belonging to the D_{2d} 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^{-1} width.

Table 1: Frequencies ω and ω' in cm^{-1} , Duschinsky transformation matrix \mathbf{J} and normal mode displacements \mathbf{K} ($\text{\AA} \cdot \text{amu}^{1/2}$) for the five mode model system.

ω'	ω	mode	\mathbf{J}					\mathbf{K}
			ν'_1	ν'_2	ν'_3	ν'_4	ν'_5	
1484	1500	ν_1	0.97	0.20	0.15	-0.04	-0.05	0.507
1314	963	ν_2	0.10	-0.82	-0.03	-0.13	0.00	0.210
714	668	ν_3	-0.02	-0.01	-1.00	0.11	-0.03	0.580
615	488	ν_4	-0.14	0.16	-0.13	-0.81	-0.01	0.236
370	390	ν_5	0.03	0.16	-0.00	0.05	1.03	0.981