On the application of separable potentials in the description of resonance fluorescence

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The formalism of scattering theory was recently applied[1] for the study of resonance fluorescence from a molecular dissociative continuum. The Born–Oppenheimer separability together with the Condon approximation allows a complete description of photon scattering from a single dissociative continuum or, more generally, from a set of uncoupled continua.[1] The explicit evaluation of the Green's function and of the reaction operator for two coupled continua, say $\{|n\rangle\}$ and $\{|m\rangle\}$ can be accomplished for separable intercontinuum interaction potentials, V, of the form $\langle n | V | m \rangle = v_1(n) v_2(m)$, or for optical potentials of the form

$$\langle n | V | n' \rangle = \sum_l (2l+1) v_1^l(n) v_1^l(n') P_l(\hat{n} \cdot \hat{n}') \ .$$

These separable potentials applied for resonance fluorescence[1] have a long history in nuclear scattering.[2] Fulton[3] has generalized our treatment to include factorized interactions

$$\langle n | V | m \rangle = \sum_{i=1}^{M} v_1^i(n) v_2^i(m) \ ,$$

suggesting that his solutions can be applied to dispense with the Condon approximation. We would like to point out that although Fulton's mathematical procedure is correct, his new formalism is unnecessary for the study of resonance fluorescence from a dissociative continuum in diatomics, while for polyatomic molecules, further extensions of the formalism are essential. Both in our previous treatment[1] and in Fulton's study[3] the role of rotation was not explicitly introduced. We shall provide a complete discussion of the separability of the molecular coupling with the radiation field.

In the Born–Oppenheimer approximation the general molecular wavefunction is

$$\Psi_{e\lambda}(\{r_i\}, \{R_j\}, \Theta) = \psi_e(\{r_i\}, \{R_j\}) \, \Phi_{e\lambda}(\{R_j\}, \Theta) \ ,$$

where r_i and R_j are electronic and nuclear coordinates, respectively, defined in a molecular fixed coordinate system (x, y, z) while Θ represents the three Euler angles $(\theta\varphi\chi)$ defining the orientation of the (x, y, z) frame with respect to a space fixed (XYZ) coordinate system. The origins of both coordinate systems are at the molecular center of mass. ψ_e and $\Phi_{e\lambda}$ represent electronic and total vibrational–rotational wavefunctions, respectively. The electromagnetic interaction matrix element is given in the notation of Ref. (1) by

$$(\langle e\lambda, ke | H_{int} | e'\lambda', vac\rangle) = \beta' h(k) \sum_{\alpha=x,y,z} (\Phi_{e\lambda} \mu_{ee'}^{(\alpha)} \{R_j\} F_{\alpha e} \Phi_{e'\lambda'})$$

$$(1)$$

where μ is the transition moment operator in the molecular fixed frame

$$\mu_{ee'}\{R_j\} = \langle \psi_e | \mu | \psi_{e'} \rangle \equiv \mu_{ee'}^{(\alpha)}, \ \alpha = x, y, z \ .$$

( ) and $\langle \ \rangle$ refer to integrations over nuclear and electronic coordinates, respectively, while $F(\theta\varphi\chi)$ corresponds to a transformation matrix between the molecule fixed and space fixed coordination systems.

Specializing these results to diatomics[4] we take for the bound state $|e\lambda\rangle \equiv |gv\Lambda JM\rangle = \varphi_g(\{r_i\}, R)\chi_v^{J\Lambda}(R) D_{M\Lambda}^J(\varphi\theta 0)$ while for the continuum dissociative state $|e'\lambda'\rangle \equiv |l\epsilon\Lambda'J'M'\rangle = \varphi_l(\{r_i\}, R)\epsilon^{J'\Lambda'}(R)D_{M'\Lambda'}^{J'}(\varphi\theta 0)$. Here Λ is the angular momentum component along the molecular axis whereas JM are the total angular momentum quantum numbers with respect to the space fixed axes. $\chi_v^{J\Lambda}(R)$ is the vibrational wavefunction, $\epsilon^{J'\Lambda'}(R)$ represents the continuum dissociative nuclear wavefunction while $D_{\Lambda M}^J(\varphi\theta 0)$ is a Wigner rotation matrix. For parallel type transitions $\mu_{gl}^{(x)}(R) = \mu_{gl}^{(y)}(R) = 0$ and $\mu_{gl}^{(z)}(R) \neq 0$ while for perpendicular type transitions $\mu_{gl}^{(x)}(R) = \mu_{gl}^{(y)}(R)$ and $\mu_{gl}^{(z)} = 0$ for all values of the internuclear separation R. Thus for diatomic Eq. (1) yields

$$(\langle gv\Lambda JM, ke | H_{int} | l\epsilon\Lambda'J'M', vac\rangle)$$

$$= \beta' h(k)(\chi_v^{J\Lambda} | \mu_{gl}^{(z)}(R) | \epsilon^{J'\Lambda'})(D_{M\Lambda}^J | F_{gZ} | D_{M'\Lambda'}^{J'})$$

for parallel transitions

$$= \beta' h(k)(\chi_v^{J\Lambda} | \mu_{gl}^{(x)}(R) | \epsilon^{J'\Lambda'})(D_{M\Lambda}^J | F_{xZ} + F_{yZ} | D_{M'\Lambda'}^{J'})$$

for perpendicular transitions. $\qquad$ (2)

Adopting the "axial recoil"[5] approximation, i.e., ignoring the weak J dependence of $\chi_v^{J\Lambda}$ and $\epsilon^{J'\Lambda'}$ for a narrow J range ($\Delta J = \pm 1$) we see that the interaction (2) is separable and we can use Eq. (II. 19) of Ref. (1) replacing $f_v(E_l)$ [Eq. (II. 20) of Ref. (1)] by the generalized Franck Franck–Condon factors $f_v^{\Lambda\Lambda'}(\epsilon) = (\chi_v^{\Delta J} | \mu_{gl}^{(\alpha)}(R) | \epsilon^{J'\Lambda'})$ which now incorporate the possible effect of the R dependence of the electronic transition moment. With the interaction (2) we can then utilize our original treatment[1] although the Condon approximation is not invoked and thus Fulton's amendment is unnecessary.

Explicit evaluation of the various cross sections using Eq. (2) requires, however, carrying out summations over M and M', which was avoided in Ref. (1) by adopting a semiclassical procedure resulting in averaging over molecular orientations. For the calculation at integrated cross sections, the semiclassical and the quantum treatments are equivalent.

Resonance scattering from polyatomics involves dissociation into a manifold of coupled intramolecular con-

tinua,[6] each corresponding to a different vibrational state of the polyatomic fragments and so the treatment of Ref. (1) must be extended. The dependence of the direction of the electronic transition moment on the nuclear configuration in polyatomics can be encountered for some weakly allowed transitions which have a considerable ingredient of vibronically induced intensity.[7] We are not familiar with the observation of such effect in bound–continuum transitions.

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[4]To avoid unnecessary complications, we consider singlet molecular terms, but our arguments may be easily extended for multiplet molecular states.

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