SAND2012-7390C

A scaling rule for the collision energy dependence of a rotationally inelastic differential cross-section: a case study of NO(X) + He

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Method:

Exact Quantum Treatment(QM): Solve large sets(>1000) of coupled differential equations that contain all the relevant scattering channels *j, l, Ω, ε* to result the T matrix $T^{J}_{j',l',\Omega',\varepsilon';j,l,\Omega,\varepsilon}$ scattering process at each *J* and parity. In our case one has to do this for *J* =0.5 up to J=120.5. This all requires a state of the art computational effort!

Quasi-Quantum Treatment (QQT): employs a Feynman path alike integral over the angular variables in the kinematic apse frame. *QQT* assigns a phase factor to each scattering (ray) trajectory according its path length and its De Broglie wavelength. As a result the *QQT* provides a valuable physical insight while requiring very little computa-tional effort[1,2]. The *QQT* scattering amplitude follows from:

$$g(\beta,p;j',m'_a \leftarrow j=0,m_a)=C(\beta)<j',m'_a\,|\,g_{geom}(\gamma_a;\beta)\cdot\exp[i\eta_{j'\leftarrow j}(\gamma_a;\beta)]\,|\,j=0,m_a> \quad (1)$$

where the phase shift is:

$$\eta_{f\leftarrow i}(\gamma_a;\beta,p)=-\boldsymbol{a}(\beta,p)\cdot\boldsymbol{R}_S(\gamma_a)=-[k_\perp-(-1)^p k'_\perp]\cdot R_S(\gamma_R)\cdot\cos(\gamma_R-\gamma_a) \quad (2)$$

and the geometric scattering amplitude is:

$$g_{geom}(\gamma_a;\beta)\equiv k\sqrt{\frac{d\sigma^{geom}(\gamma_a;\beta)}{d\omega_a}}=k\sqrt{|\cos\beta\,|\cdot\rho_1(\gamma_a)\cdot\rho_2(\gamma_a)} \quad (3)$$

An important difference between the *QM* and *QQT* treatment is that the former is addressed in the collision frame, the state-to-state DCS is described by the spherical angles *θ*, while the latter is addressed in the kinematic apse frame, where the DCS is given by the spherical angles *β*.

Extension of QQT into the classically forbidden region:

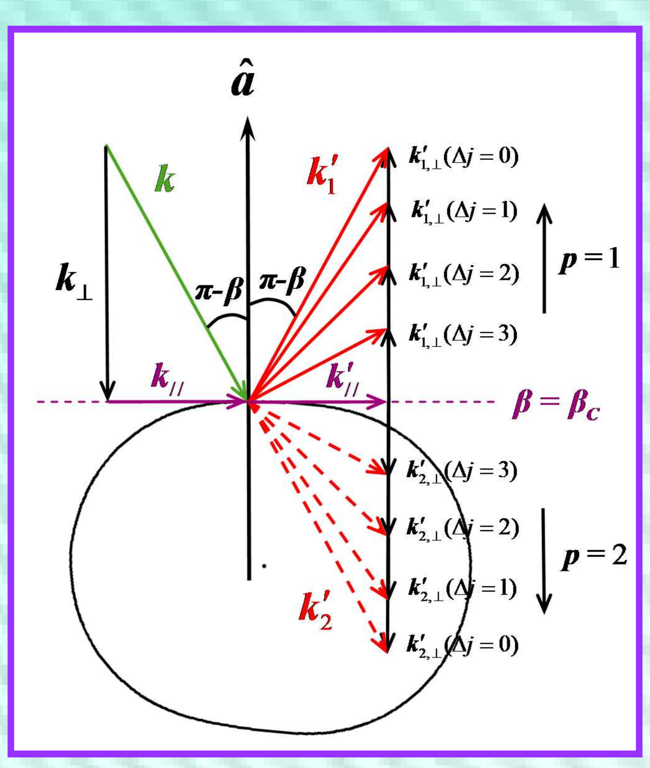

Fig.1. *Representation of the classically allowed (solid lines) and classically forbidden (dashed lines) Feynman paths that contribute to the scattering amplitude within the QQT formalisms.*

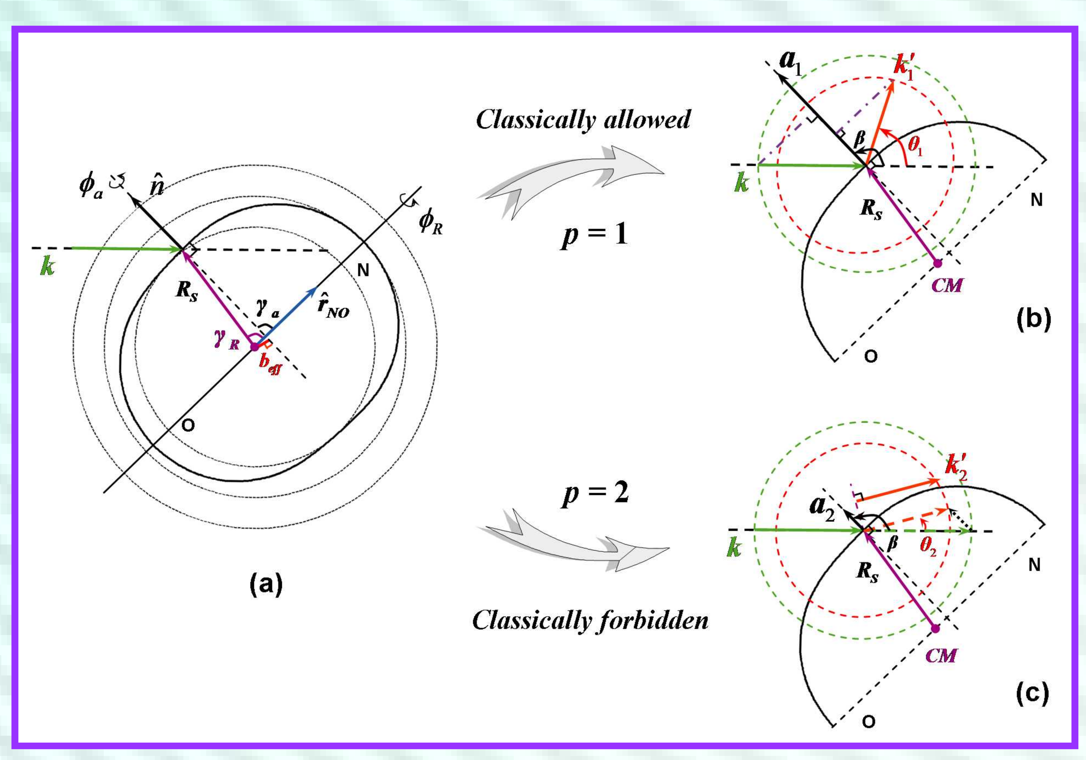

Fig.2 *Representation of the angles defining the QQT collision geometry (left hand panel), and the classically allowed (upper right hand panel) and classically forbidden (lower right hand panel) Feynman paths that contribute to the scattering amplitude within the QQT formalism.*

Scaling process:

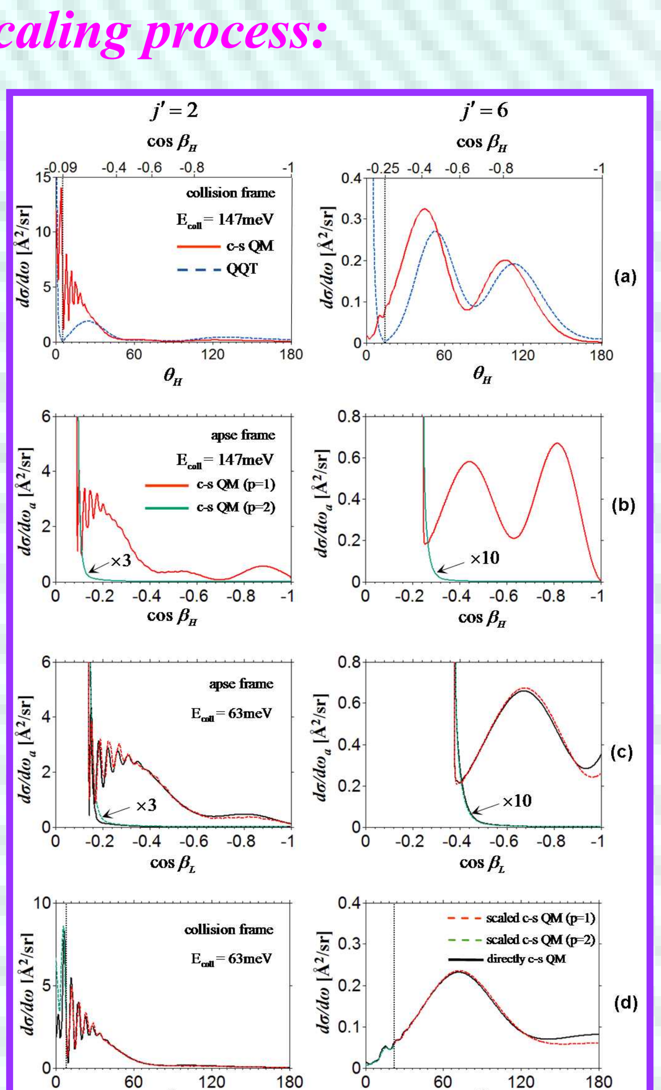

Fig.3. *Illustration of the step-by-step process used to scale the closed-shell QM DCSs from a high collision energy E_H to a lower collision energy E_L. The scattering of NO(X)+He from j=0 to j'=2 and to j'=6 are considered as examples here.*

The relation between the scattering angle θ and apse angle β is:

$$\cos\beta=\hat{\boldsymbol{a}}\cdot\hat{\boldsymbol{Z}}=\frac{k'\cos\theta-k}{\sqrt{k'^2-2kk'\cos\theta+k^2}} \quad (4)$$

$$\theta=\arccos\left[\left(\frac{k}{k'}\right)\sin^2\beta\;+(-1)^p\,|\cos\beta\,|\left(1-\left(\frac{k}{k'}\right)^2[\sin^2\beta]\right)^{0.5}\right] \quad (5)$$

the cutoff angle is:

$$-1\le\cos\beta\le\cos\beta_c=-\sqrt{1-(k'/k)^2} \quad (6)$$

The relation between the apse and collsion frame is:

$$\frac{d\sigma_{f\leftarrow i}}{d\omega}(\theta,\phi)=\frac{d\sigma_{f\leftarrow i}}{d\omega_a}(\beta,\alpha)\cdot\left|\frac{d\cos\beta(\theta)}{d\cos\theta}\right| \quad (7)$$

where:

$$\frac{d\cos\beta}{d\cos\theta}=\frac{(k')^2\cdot[k'-k\cos\theta]}{\{(k')^2-2kk'\cos\theta+k^2\}^{1.5}} \quad (8)$$

The phase shift, geometry scattering amplitude and the differential cross section calcualted at collision energy of E_H and E_L relates to each other by:

$$g^L_{geom}(\gamma_a;\cos\beta_L)=\sqrt{\frac{k_L}{k_H}}\,g^H_{geom}(\gamma_a;\cos\beta_H=\tfrac{k_L}{k_H}\cdot\cos\beta_L) \quad (9)$$

$$\eta^L_{f\leftarrow i}(\gamma_a;\cos\beta_L,p)=\eta^H_{f\leftarrow i}(\gamma_a;\cos\beta_H=\tfrac{k_L}{k_H}\cdot\cos\beta_L,p) \quad (10)$$

$$\frac{d\sigma^{QQT;L}_{f\leftarrow i}(\cos\beta_L)}{d\omega_a}=\frac{k_H}{k_L}\frac{d\sigma^{QQT;H}_{f\leftarrow i}(\cos\beta_H=\tfrac{k_L}{k_H}\cos\beta_L)}{d\omega_a} \quad (11)$$

Results:

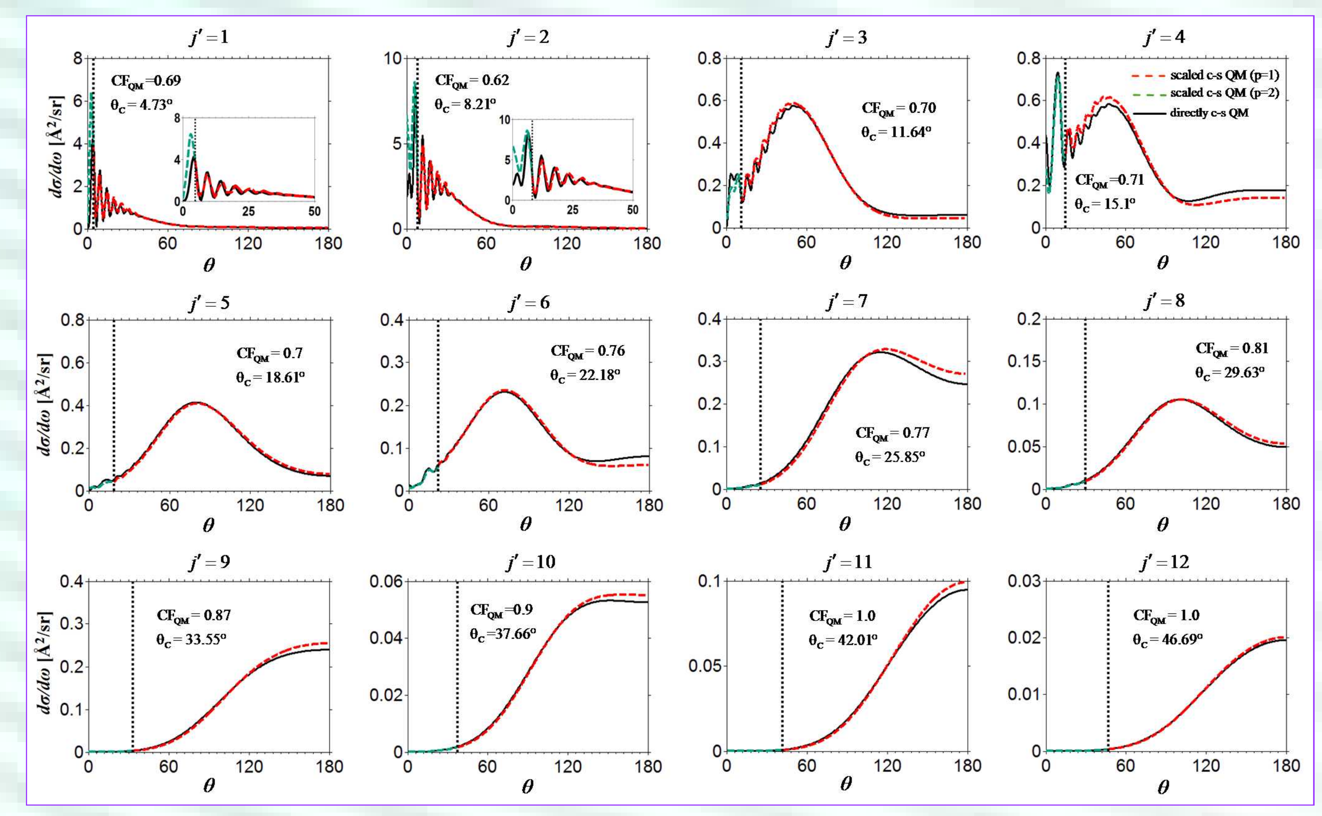

Fig.4. *Complete set of results for the comparison of the* ***closed-shell QM*** *NO(X)+He DCSs from initial state j=0 to final states j'=1-12 scaled from a collision energy of 147meV to 63meV (dashed lines) with those DCSs calculated directly at 63meV (solid lines). Insets in the first two panels show a detailed comparison at low scattering angles. The point at which each transition becomes classically forbidden is shown as a dashed vertical line.*

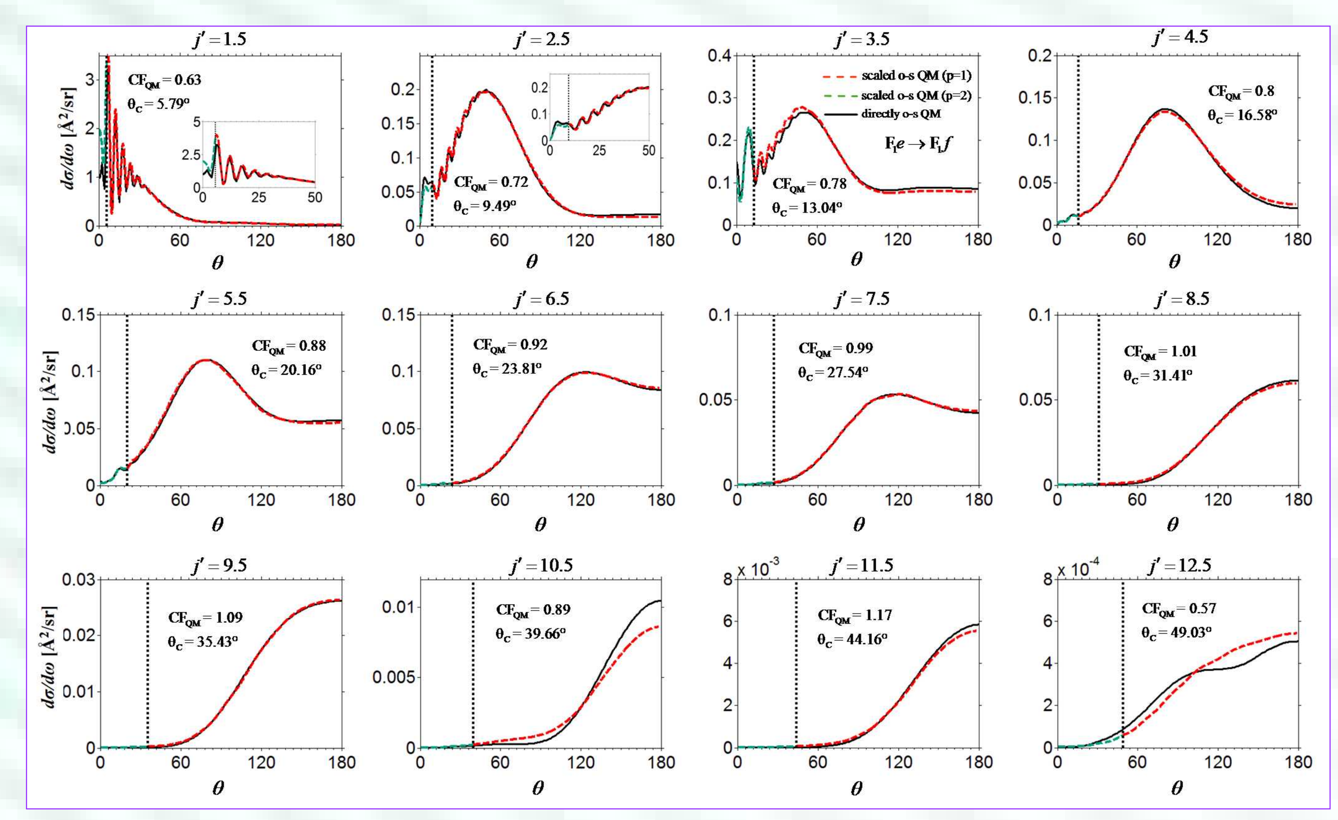

Fig.5. *Complete set of results for the comparison of the* ***open-shell spin-orbit conserving QM*** *NO(X)+He DCSs from initial state j=0.5, e to final states j'=1.5-12.5, f scaled from a collision energy of 147meV to 63meV (solid lines) with those DCSs calculated directly at 63meV (dashed lines). Insets in the first two panels show a detailed comparison at low scattering angles.*

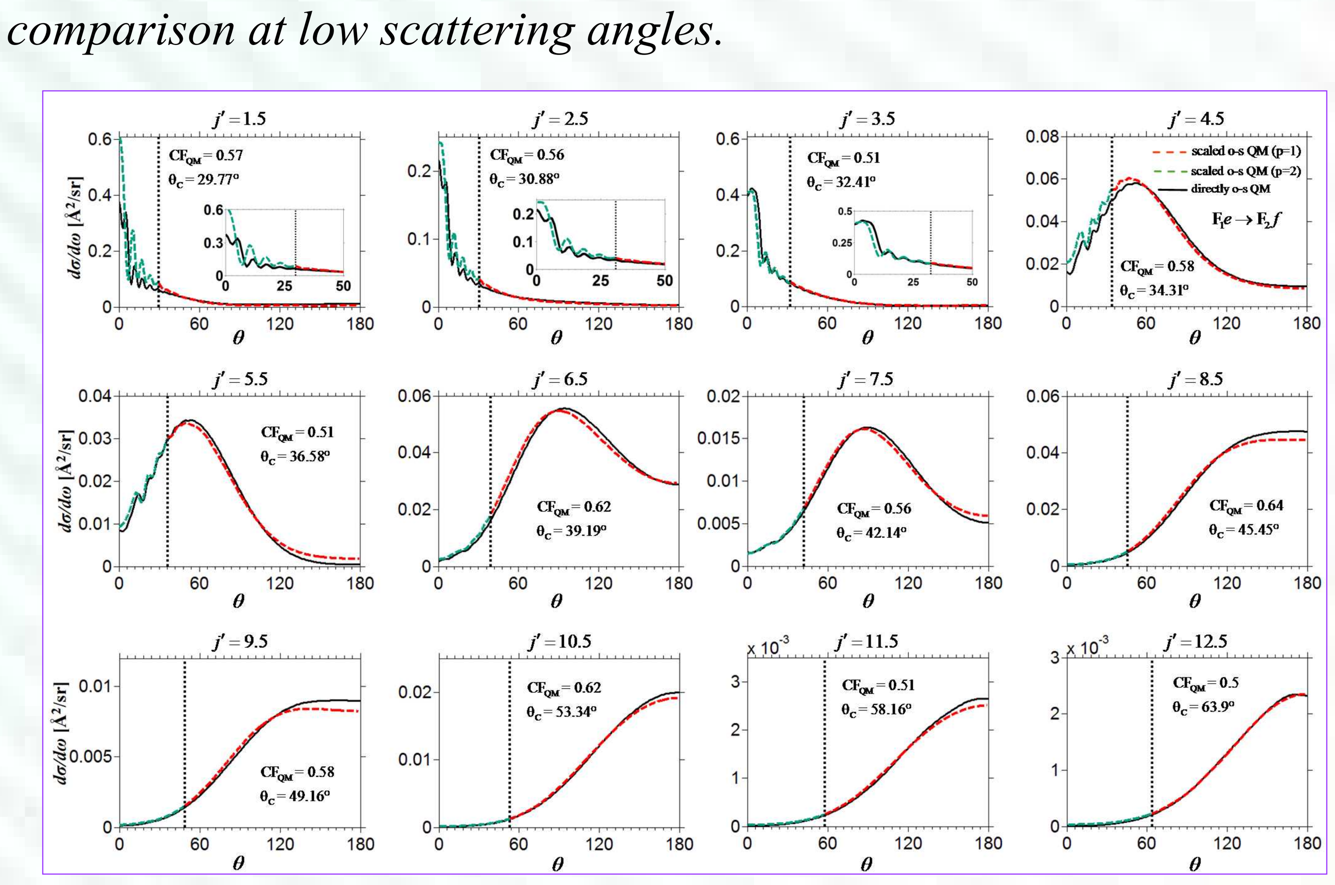

Fig.6. *same as fig.5 but for the* ***open-shell spin-orbit changing QM*** *NO(X)+He DCSs transition from e⟶ f*

References:

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