Appendices

I.A – The stationary nature of the QQT collision frame and apse frame DCS at $\theta = 0$ and $\theta = \pi$

The azimuthal symmetry of the DCS constrains its mathematical form to be stationary at $\theta = 0$ and $\theta = \pi$ in the scattering frame and in the apse frame. In this appendix we prove that these conditions are indeed fulfilled within the QQT framework. As previously noted, the QM DCSs automatically fulfill this requirement in the collision frame, because they can be written as a series of Legendre polynomials, all of which individually meet this criterion. When transformed into the apse frame, the constraints are then met in the same fashion as the QQT DCSs.

As a starting point we shall consider the QQT DCS in the apse frame. From eq 9 one writes the QQT apse-frame scattering amplitude as

$$\frac{g_{j',m_a' \leftarrow j=0,m_a}(\theta)}{C(\theta)} = < j',m_a' \mid g_{geom}(\theta) \cdot P_{j'}(\cos\gamma_a) \cdot \exp[i\eta_{j'\leftarrow j=0}(\theta)] \mid j=0,m_a > \tag{I.1}$$

where the dependence of all quantities in eq I.1 on θ has been made explicit. Equation 10 can be used to write out the θ dependence of the phase shift, η, as

$$\eta_{j'\leftarrow j=0}(\theta) = \sqrt{k^2 + k'^2 - 2kk'\cos\theta} \cdot A(\gamma_a) \tag{I.2}$$

where $A(\gamma_a)$ is independent of θ (and hence does not affect the behavior of the DCS as a function of θ). We now turn our attention to the first stationary point, located at $\theta = 0$. Around this region, one can neglect all but the leading terms in the Taylor expansion of $\cos\theta$, such that

$$\cos\theta \cong 1 - \frac{\theta^2}{2} \tag{I.3}$$

Utilizing eq I.3 then allows us to approximate the $\cos\theta$ dependence of eq I.2 in the forward scattered direction to

$$\eta_{j'\leftarrow j=0}(\theta) = \sqrt{k^2 + k'^2 - 2kk' + kk'\theta^2} \cdot A(\gamma_a)$$
$$\cong \left(k - k' + \frac{kk'\theta^2}{2(k-k')^2} \right) \cdot A(\gamma_a) \tag{I.4}$$

Note that the last line of eq I.4 is obtained by performing a Taylor expansion of $(1+a\theta^2)^{1/2}$, about $a\theta^2 = 0$, keeping only the leading term in $a\theta^2$. The behavior of the exponential part of eq I.1 around $\theta = 0$ can then be written as

$$\exp[i\eta_{j'\leftarrow j=0}(\theta \to 0)] = \exp[i\eta_{j'\leftarrow j=0}(\theta = 0)] \cdot \exp\left[\frac{ikk'\theta^2}{2(k-k')^2}\right] \cdot A(\gamma_a) \tag{I.5}$$

Taking the derivative of eq I.5 with respect to θ and evaluating as θ tends to zero then yields

$$\frac{d\exp[i\eta_{j'\leftarrow j=0}(\theta \to 0)]}{d\theta} = \exp[i\eta_{j'\leftarrow j=0}(\theta = 0)] \cdot \exp\left[\frac{ikk'\theta^2}{2(k-k')^2}\right] \cdot \frac{kk'\theta}{(k-k')^2} \cdot A(\gamma_a) = 0 \tag{I.6}$$

At the second stationary point, where $\theta \to \pi$, $\cos\theta$ can instead be approximated by

$$\cos\theta \cong -1 + \frac{(\pi-\theta)^2}{2} \tag{I.7}$$

Using the same arguments as were employed for the case of $\theta = 0$, it can be shown that

$$\frac{d\exp[i\eta_{j'\leftarrow j=0}(\theta \to \pi)]}{d\theta} = 0 \tag{I.8}$$

when $\theta = \pi$ also. The exponential part of the QQT apse frame scattering amplitude has thus been shown to go to zero as θ goes to 0 or π, as required.

The non-exponential part of eq I.1 can also be differentiated with respect to θ, in this case yielding the expression

$$\frac{dg_{geom}(\theta)}{d\theta} = \rho_1(\gamma_a) \cdot \rho_{12}(\gamma_a) \frac{d}{d\theta}|\cos\beta| = \rho_1(\gamma_a) \cdot \rho_2(\gamma_a) \frac{d|\cos\beta|}{d\cos\theta} \cdot \frac{d\cos\theta}{d\theta} \tag{I.9}$$

Since $\cos\theta$ is obviously stationary at $\theta = 0$ and $\theta = \pi$, the geometric scattering amplitude must also display the same behavior, such that

$$\frac{dg_{geom}(\theta \to 0, \pi)}{d\theta} = 0 \tag{I.10}$$

eqs I.6, I.8, and I.10 can then be jointly substituted into eq I.1 to yield the required behavior in the apse frame

$$\frac{dg_{j',m'_a \leftarrow j=0,m_a}(\theta = 0, \pi)/C(\theta)}{d\theta} = \frac{dg_{j',m'_a \leftarrow j=0,m_a}(\beta = \pi, p = 1, 2)/C(\beta)}{d\theta} = 0 \tag{I.11}$$

Additionally it can be shown (by summing the scattering amplitude over all final states) that the first derivative of the normalization constant, $C(\beta)$, with respect to β is also equal to zero

$$\frac{dC(\beta = \pi)}{d\beta} = 0 \tag{I.12}$$

Combining eqs I.1, I.11, and I.12, the first derivatives of the QQT DCSs in the apse frame must also necessarily be stationary at $\theta = 0, \pi$ as is required:

$$\frac{\mathrm{d}^2\sigma_{j'\leftarrow 0}^{QQT}}{\mathrm{d}\omega_a\mathrm{d}\theta}(\theta=0,\pi)=\frac{\mathrm{d}^2\sigma_{j'\leftarrow 0}^{QQT}}{\mathrm{d}\omega_a\mathrm{d}\theta}(\beta=\pi,p=1,2)=0 \tag{I.13}$$

Note that eq 14 relates the QQT collision frame DCSs to its apse frame counterpart, hence:

$$\frac{\mathrm{d}^2\sigma_{j'\leftarrow 0}^{QQT}}{\mathrm{d}\theta\cdot\mathrm{d}\omega}(\theta,\phi)=\frac{\mathrm{d}\sigma_{j'\leftarrow 0}^{QQT}}{\mathrm{d}\theta\cdot\mathrm{d}\omega_a}(\beta,p)\cdot\left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right|+\frac{\mathrm{d}\sigma_{j'\leftarrow 0}^{QQT}}{\mathrm{d}\omega_a}(\beta,p)\cdot\frac{\mathrm{d}}{\mathrm{d}\theta}\left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right| \tag{I.14}$$

As was shown in eq 19, setting θ equal to 0 or π gives us the simple relations

$$\left|\frac{\mathrm{d}\cos\beta(\theta=0)}{\mathrm{d}\cos\theta}\right|=\frac{1}{(1-k/k')^2} \tag{I.15}$$

$$\left|\frac{\mathrm{d}\cos\beta(\theta=\pi)}{\mathrm{d}\cos\theta}\right|=\frac{1}{(1+k/k')^2} \tag{I.16}$$

which leads to:

$$\frac{\mathrm{d}^2\sigma_{j'\leftarrow 0}^{QQT}}{\mathrm{d}\theta\cdot\mathrm{d}\omega_a}(\beta=\pi,p=1,2)\cdot\left|\frac{\mathrm{d}\cos\beta(\theta=0,\pi)}{\mathrm{d}\cos\theta}\right|=0 \tag{I.17}$$

Finally

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right|=\left\{\mathrm{d}\frac{(k')^2\cdot[k'-k\cos\theta]}{[(k')^2-2kk'\cos\theta+k^2]^{1.5}}\Big/\mathrm{d}\cos\theta\right\}\cdot\frac{\mathrm{d}\cos\theta}{\mathrm{d}\theta} \tag{I.18}$$

Note that I.18 is zero for $\theta=0$ and for $\theta=\pi$.

Combining eqs I.14, I.17, and I.18, the first derivatives of the QQT DCSs in the collision frame are stationary at $\theta=0,\pi$.

I.B – The stationary nature of the QM apse frame and collision frame DCS at $\theta=0$ and $\theta=\pi$

Arthurs and Dalgarno[1] showed that

$$\frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{QM}}{\mathrm{d}\omega}(\hat{\boldsymbol{k}}'\cdot\hat{\boldsymbol{k}})\propto\sum_{\lambda=0}^{\infty}A_\lambda\cdot P_\lambda(\hat{\boldsymbol{k}}'\cdot\hat{\boldsymbol{k}}) \tag{I.19}$$

which implies that at $\theta=0$ or $\theta=\pi$,

$$\frac{\mathrm{d}}{\mathrm{d}\theta}\frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{QM}}{\mathrm{d}\omega}(\hat{\boldsymbol{k}}'\cdot\hat{\boldsymbol{k}})=0 \tag{I.20}$$

eq 14 can also be applied to relate the QM collision frame DCSs to its apse frame counterpart:

$$\frac{\mathrm{d}^2\sigma_{j',f\leftarrow j,i}^{QM}}{\mathrm{d}\theta\cdot\mathrm{d}\omega_a}(\theta,\varphi)=\frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{QM}}{\mathrm{d}\theta\cdot\mathrm{d}\omega}(\beta,p)\cdot\left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right|^{-1}+\frac{\mathrm{d}\sigma_{j',f\leftarrow j,i}^{QM}}{\mathrm{d}\omega_a}(\beta,p)\cdot\frac{\mathrm{d}}{\mathrm{d}\theta}\left|\frac{\mathrm{d}\cos\beta(\theta)}{\mathrm{d}\cos\theta}\right|^{-1} \tag{I.21}$$

Inspection of eq I.18 and combining with eqs I.20, I.21 shows that $\dfrac{\mathrm{d}^2\sigma^{QM}_{j',f\leftarrow j,i}}{\mathrm{d}\theta\cdot\mathrm{d}\omega_a}(\theta,\varphi)=0$ if $\theta=0$ or

$\theta=\pi$.

Table I: Numerical values of the closed-shell QQT NO(X)+He DCSs from $j=0$ to $j'=1-12$ at a collision energy of $E^L_{col}=63\mathrm{meV}$ for $\theta=0$ and $\theta=\pi$. Values are given in both the kinematic apse and the collision frames.

	$\mathrm{d}\sigma/\mathrm{d}\omega_a$ (β) (Å²/sr)		$\mathrm{d}\sigma/\mathrm{d}\omega$ (θ) (Å²/sr)	
j'	$\theta=0$	$\theta=\pi$	$\theta=0$	$\theta=\pi$
1	3.83E-05	0.192	3.682	0.054
2	0.0515	0.104	538.25	0.029
3	0.0028	0.281	7.064	0.077
4	0.0605	0.527	52.81	0.142
5	0.0045	0.575	1.653	0.152
6	0.0375	0.280	6.555	0.072
7	0.0052	1.343	0.468	0.337
8	0.0244	0.354	1.208	0.086
9	0.0056	1.059	0.157	0.245
10	0.0163	0.343	0.263	0.075
11	0.0058	0.357	0.054	0.073
12	0.0111	0.135	0.059	0.025

II – The angular momentum wave function of the open-shell ground state NO(X) Molecule

The open-shell ground state $\mathrm{NO(X^2\Pi)}$ molecule possesses one unpaired electron in its lowest anti-bonding Π orbital. This gives rise to a projection of the electronic orbital angular momentum, $\mathbf{L}$, onto the inter-nuclear axis specified by the angular momentum quantum number $\Lambda=\pm1$. In the limit where Hund's case (a) applies exactly, the unpaired electron spin $\mathbf{S}=\frac{1}{2}$ makes a further projection onto the inter-nuclear axis characterized by the quantum number $\Sigma=\pm\frac{1}{2}$ The total projection of $\mathbf{j}=\mathbf{L}+\mathbf{S}$ onto the inter-nuclear axis is then characterized by the quantum number $\Omega\equiv\Lambda+\Sigma$.

This coupling of angular momenta gives rise to two spin-orbit states, $\overline{\Omega}=\frac{1}{2}$ and $\overline{\Omega}=\frac{3}{2}$, where

$\bar{\Omega} \equiv |\Omega| = \frac{1}{2}$ is the ground spin-orbit state due to the positive spin-orbit constant of $A_0 = 123.13 \text{cm}^{-1}$ associated with the NO molecule.[2] As long as the pure rotational energy of the NO molecule, given by $H_{rot} = B_0(\boldsymbol{j} - \boldsymbol{S} - \boldsymbol{L})^2$ (where $B_0 = 1.6961 \text{cm}^{-1}$)^2 is much smaller than the energy difference between the two spin-orbit channels, given by $H_{SO} = A_0 \boldsymbol{L} \cdot \boldsymbol{S}$, then the angular momentum eigenfunctions of the NO molecule can be written as

$$| j,m,\bar{\Omega},\varepsilon > = \frac{1}{\sqrt{2}}\{| j,m,\bar{\Omega} > + \varepsilon | j,m,-\bar{\Omega} > \qquad (\text{II.1})$$

Note that the quantum state (projection) numbers, Λ and Σ, are implicitly defined since when $\Omega = \pm\frac{1}{2}$ one has $\Sigma = \mp\frac{1}{2}$, $\Lambda = \pm 1$, while when $\Omega = \pm\frac{3}{2}$ one has instead $\Sigma = \pm\frac{1}{2}$, $\Lambda = \pm 1$. So in the case of a signed value of Ω the quantum numbers Σ and Λ are uniquely determined and are therefore omitted in eq (II.1). The parity of the NO molecular rotational wavefunction is denoted with the spectroscopic parity index $\varepsilon = \pm 1$, such that the parity is given by $p = (-1)^{j-\varepsilon/2}$. The interaction with electronically excited states, or the reduction in symmetry arising from the approach of a collision partner, leads to a further Λ-doublet splitting of the rotational energy levels. In the case of the NO molecule, this gives rise to a small positive energy shift (typically $\ll 1\text{cm}^{-1}$) of the $\varepsilon = -1$ or spectroscopic f-labeled states with respect to the $\varepsilon = 1$ or spectroscopic e-labeled states.

For higher rotational states, around $j > 7.5$, the rotational energy splitting become significant compared to the spin-orbit energy splitting, and the coupling of the angular momenta within the NO molecule is no longer well described by Hund's case (a). The two spin-orbit channels become mixed, where the probability amplitude[3]

$$b_j = \sqrt{\frac{1}{2}[1 - \frac{A_0/B_0 - 2}{[4(j+\frac{1}{2})^2 + (A_0/B_0)^2 - 4A_0/B_0]^{0.5}}]} \qquad (\text{II.2})$$

quantifies the degree of mixing between the spin-orbit ground $\bar{\Omega} = \frac{1}{2}$ and exited $\bar{\Omega} = \frac{3}{2}$ states. As an example, for the rotational state $j = 8.5$, this probability amplitude takes a value of $b_{j=8.5} = 0.1238$. The wavefunctions of the NO molecule must now be written as a linear combination of the two spin-orbit eigenstates, such that the lower spin-orbit channel is now given by

$$| F_1, j,m,\varepsilon > = \sqrt{1 - b_j^2} \cdot | j,m,\bar{\Omega} = \frac{1}{2},\varepsilon > + b_j \cdot | j,m,\bar{\Omega} = \frac{3}{2},\varepsilon > \qquad (\text{II.3})$$

and the upper spin-orbit channel by

$$| F_2, j, m, \varepsilon >= \sqrt{1-b_j^2} \cdot | j, m, \bar{\Omega} = \tfrac{3}{2}, \varepsilon > - b_j \cdot | j, m, \bar{\Omega} = \tfrac{1}{2}, \varepsilon > \qquad \text{(II.4)}$$

The mixed spin-orbit states specified by the indices F_1 and F_2 lead to an additional physical interpretation of the symmetry label specifying the Λ-doublet level. For the ground spin-orbit state, the $\varepsilon = -1$ (or f) label corresponds to A'' symmetry, in which the molecular wavefunction is anti-symmetric with respect to reflection in the plane of rotation, while the $\varepsilon = 1$ (e) label indicates A' symmetry, in which the molecular wavefunction is symmetric with respect to this reflection (this ordering is then reversed for the upper spin-orbit state). In the classical high-j limit, these labels correspond to the case in which the electron in the unpaired Π^* orbital lies either out of ($\varepsilon = -1$ or f), or in the plane of rotation ($\varepsilon = 1$ or e) of the NO molecule.

References:

(1)   Arthurs, A. M.; Dalgarno, A. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **1960**, *256*, 540.

(2)   Amiot, C. *Journal of Molecular Spectroscopy* **1982**, *94*, 150.

(3)   Zare, R. N. *Angular Momentum: Understanding Spatial Aspects in Chemistry and Physics*; John Wiley & Sons: New York, 1988.