On a Field-Theoretic Formulation of Scaling Laws in Molecular Scattering

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Vibro-rotational excitation processes, in particle-diatom scattering, are considered from a field-theoretical point of view. It is shown that a relaxation of the relationship directly connecting boundary conditions and reference state, of the Green's functions of the theory, can lead to a formulation of ab initio "scaling laws", for both elastic and inelastic scattering.

1. Statement of the Problem

The applicability of field-theoretic (FT) techniques to low energy atomic and molecular scattering has recently been illustrated [1–4]. For molecules, the wealth of internal vibro-rotational states makes it desirable to find "rigorous" procedures, whereby information relative to a particular transition can (partially or totally) be used for elucidating different processes as well. The present communication is therefore intended to point out how FT techniques might help in obtaining such ab initio "scaling laws" in low energy molecular scattering.

We shall consider, specifically, a collision between a particle (A) and a diatomic species (BC), of the kind

$$A\,(k_i) + BC\,(i) \begin{cases} \rightarrow A\,(k_i) + BC\,(i) \ \text{elastic}, & (1\,\text{a}) \\ \rightarrow A\,(k_f) + BC\,(f) \ \text{inelastic}. & (1\,\text{b}) \end{cases}$$

In (1a)–(1b) "k" labels the momentum of A, while "i" and "f" refer to the internal states of BC. It has been shown [1] that the S-matrix of the elastic process, (1a) above, is related to the following FT amplitude

$$S_{ii} \cong \langle i \,|\, T[\psi\,\psi^\dagger] \,|\, i \rangle = i\,G^i(\varepsilon_i)\,. \tag{2}$$

where $|\,i\rangle$ refers to the i-th vibro-rotational molecular level, G^i is the one-particle Green's function for the A species (ψ, $\psi^\dagger$ are destruction, creation field operators for A) and the proportionality sign in (2) takes care of things such as time limits and spatial integrations. G^i satisfies, in turn, Dyson's equation [5]

$$\{[G^0(\varepsilon_i)]^{-1} - \Sigma^i(\varepsilon_i)\}\, G^i(\varepsilon_i) = \underset{\sim}{1} \tag{3}$$

at the $\varepsilon_i = \hbar^2 k_i^2 / 2m$ scattering energy. G^0 in (3) is the unperturbed Green's function and Σ represents the "optical potential", presiding over elastic processes. In particular, in an approximation of the second order with respect to the subsystems interaction potential, V, we have

$$\begin{aligned} \Sigma^i(\varepsilon_i) &\cong \Sigma^{i(1)}(\varepsilon_i) \\ &= \underset{\sim}{1} \cdot V_{ii} + \sum_{n \neq i} V_{in}\, G^i(\varepsilon_i - \omega_{ni})\, V_{ni}\,. \end{aligned} \tag{4}$$

We have put, in (4), $V_{ij} = \langle i \,|\, V \,|\, j \rangle$ and $\omega_{ij} = \omega_i - \omega_j$, the energy difference between the corresponding target states. Acting on (3) with a suitable (Gell-Mann and Low) operation [6], we obtain an equation that (to second order in V) "completely" determines elastic scattering. In integral form this is given by

$$|\, f^i_{k_i} \rangle = |\, \Phi_{k_i} \rangle + G^0(\varepsilon_i)\, \Sigma^{i(1)}(\varepsilon_i) \,|\, f^i_{k_i} \rangle\,. \tag{5}$$

Inelastic transitions are next defined by

$$T_{fi} = \langle f^i_{k_f} \,|\, V^i_{f \leftarrow i} [(\varepsilon_f + \varepsilon_i)/2] \,|\, f^i_{k_i} \rangle \tag{6}$$

with the $V^i_{f \leftarrow i}$ "transition potential" being given, up to second order in V, by

$$\begin{aligned} V^i_{f \leftarrow i}[(\varepsilon_f + \varepsilon_i)/2] &\cong V^{i(1)}_{f \leftarrow i}[(\varepsilon_f + \varepsilon_i)/2] \\ &= -\underset{\sim}{1} \cdot V_{fi} - \sum_{n \neq f, i} V_{fn}\, G^i(\varepsilon_i - \omega_{ni})\, V_{ni} \\ &\quad - [V_{ff} - V_{ii}]\, G^i(\varepsilon_i - \omega_{fi})\, V_{fi}\,. \end{aligned} \tag{7}$$

2. Formulation of the Scaling Laws

Equation (5) is peculiar to scattering off the i-th target state, which has automatically been singled out by our boundary conditions, in (2). If we desire to pursue further our idea of scaling, we have to look, instead, for a relationship of the kind

$$S_{ii} \cong [\widehat{G - L}]_{ii} \langle r \,|\, T[A] \,|\, r \rangle\,, \tag{8}$$

where A stands for a product of (more than two) field operators and $[\widehat{G-L}]_{ii}$ represents a convenient Gell-Mann and Low "cut" operation. Equation (8), though formally more complicated than (2), might be more useful numerically. In fact, the solution of the elastic scattering problem through (8) requires a) setting up a "single" equation for the $\langle r \,|\, T[A] \,|\, r \rangle$ amplitude, where $|\, r\rangle$

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is not necessarily related to the $|i\rangle$ and $|f\rangle$ states of (1a)–(1b); b) ensuring the correct boundary conditions by the $[\widehat{G-L}]_{ii}$ operation. It is not difficult to convince ourselves that the lowest amplitude useful for this purpose is a three-particle Green's function [7]. Detailed equations can be easily obtained, showing that (8) leads to the integral equation

$$|f^r_{k_i}\rangle = |\Phi_{k_i}\rangle + G^0(\varepsilon_i)\,\Sigma^{r(1)}(\varepsilon_i)\,|f^r_{k_i}\rangle \tag{9}$$

which is identical to (5), except for $|r\rangle$ being now the reference state of all the amplitudes of the theory. Consequently, $|f^r_{k_i}\rangle$ does not contain anymore the full elastic scattering information and it can be shown that the solution to (9) must, in this case, be augmented by the evaluation of the $\tilde{S}_{ii}$ matrix element (of the second order in V)

$$\tilde{S}_{ii} = \langle f^r_{k_i}|\,{}^r\Xi^{\mathrm{el}}_{i\leftarrow i}(\varepsilon_i)\,|f^r_{k_i}\rangle \tag{10}$$

with

$$\begin{aligned} {}^r\Xi^{\mathrm{el}}_{i\leftarrow i}(\varepsilon_i) = & -\underset{\sim}{1}\cdot[V_{ii}-V_{rr}] \\ & +\sum_{n\neq r} V_{rn}\,G^r(\varepsilon_i-\omega_{nr})\,V_{nr} \\ & -\sum_{n\neq i} V_{in}\,G^r(\varepsilon_i-\omega_{ni})\,V_{ni} \\ & -[V_{ii}-V_{rr}]\,G^r(\varepsilon_i)[V_{ii}-V_{rr}]\,. \end{aligned} \tag{11}$$

Notice that the particular choice $|r\rangle\equiv|i\rangle$ gives $\tilde{S}_{ii}=0$, thus regaining the result (5). The interesting new aspect of the previous relations is that the numerical quadrature in (10) can be easily performed if one knows, "once and for all", the $|f_k{}^r\rangle$ orbital. We have then been able to obtain a first scaling law for elastic processes.

Similar considerations apply to inelastic scattering. The determination of the T-matrix of interest (based on the $|r\rangle$ reference state, T^r_{fi}) can now be made by

a) solving Eq. (9) (that represents elastic scattering off the $|r\rangle$ target state) at the energy of interest;
b) calculating the matrix element

$$T^r_{fi} = \langle f^r_{k_f}|\,{}^r\Xi^{\mathrm{in}}_{f\leftarrow i}[(\varepsilon_f+\varepsilon_i)/2]\,|f^r_{k_i}\rangle \tag{12}$$

where

$$\begin{aligned} & {}^r\Xi^{\mathrm{in}}_{f\leftarrow i}[(\varepsilon_f+\varepsilon_i)/2] \\ & \quad = -\underset{\sim}{1}\cdot V_{fi} - \sum_{n\neq i,f} V_{fn}\,G^r(\varepsilon_i-\omega_{ni})\,V_{ni} \\ & \qquad - V_{fi}\,G^r(\varepsilon_i)[V_{ii}-V_{rr}] \\ & \qquad - [V_{ff}-V_{rr}]\,G^r(\varepsilon_i-\omega_{fi})\,V_{fi}\,. \end{aligned} \tag{13}$$

If, in particular, the choice $|r\rangle\equiv|i\rangle$ is made, the result of Eq. (7) is recovered.

3. Range of Applicability

Equations (9), (10) and (12) are in the form of "ab initio" scaling laws for elastic and inelastic processes, respectively. In fact, once a $|f_k{}^r\rangle$ orbital has been determined by solving (9), this can be used in the evaluation of the T-matrix of "any" process. The corrections due to the arbitrariness in the choice of $|r\rangle$ are easily identifiable in the formulae for the Ξ^{el} and Ξ^{in} effective potentials, Eqs. (11) and (13), respectively. The only limitation inherent in Eq. (12) is that all the pairs of states to which this formula is applied be characterized by the same, ω_{fi}, energy difference. This obviously poses no limitations in a harmonic oscillator model of vibrational energy transfer. In such a case all axcitations involving the same number of quanta correspond to identical energy separations. In a more realistic description of molecules as anharmonic oscillators, we can still envision the usefulness of (12), if the "energy defect" between pairs of vibrational states is compensated by explicitly including rotational energy. In both instances, a convenient way of implementing this formalism, numerically, would be by dividing the whole molecular spectrum into a small number of portions and choosing a single reference state for each of these subsets of levels.

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