Brief Reports

Propensity rules: An analytical approach

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A structural analysis of matrix elements is used to interpret familiar propensity rules.

The concept of "propensity rule"[1] has been introduced with reference to a transition—or to a class of transitions—which is much more likely than alternative but accessible ones. Propensity thus amounts to an attenuated version of a selection rule. Selection rules result from exact symmetries or other properties of a system, propensities from less clearly identified circumstances. The original example of propensity dealt with radiative vibrational transitions with $\Delta v = 1$, which are only *favored* for a diatomic molecule in a Morse potential, in contrast to molecules with a quadratic potential that forbids $\Delta v \neq 1$ altogether.

Propensity rules occur in numerous other situations as well. Typically light absorption by atoms in transitions $l \rightarrow l+1$ is strongly favored over transitions $l \rightarrow l-1$. (In this case a sum rule provides a quantitative index of propensity.[2]) Transitions in atomic or nuclear multiparticle systems are classed as "parity favored" when their parity change is represented by $(-1)^{\Delta L}$ in terms of the change of total-orbital quantum number L. (Parity *un*favoredness generally stems from an interaction proportional of a vector product, that is, to a pseudovector of *even* parity under reflection through the origin.[3])

This note illustrates how propensity may emerge from an analysis of the structure of a relevant matrix element. For simplicity we consider here explicitly the matrix element of a radial transition operator $T(r)$,

$$\int_0^\infty dr \, \psi_f(r) T(r) \psi_i(r) , \qquad (1)$$

with WKB wave functions $\psi_{i,f} \propto \sin[\int_0^r k_{i,f}(r')dr']$,[4] but our type of analysis should apply to broader circumstances.

The essential point emerges from the trigonometric relation

$$\psi_f(r)\psi_i(r) \propto \cos\left(\int_0^r [k_f(r') - k_i(r')]dr'\right)$$
$$- \cos\left(\int_0^r [k_f(r') + k_i(r')]dr'\right) . \qquad (2)$$

The second term on the right of this formula generally oscillates rapidly and accordingly contributes but little to the integral (1). The main contribution to (1) should thus stem from whichever range of r occurs, where the product

$$T(r) \cos\left(\int_0^r [k_f(r') - k_i(r')]dr'\right) \qquad (3)$$

varies smoothly instead of oscillating.

The propensity rule favoring $l \rightarrow l+1$ for light absorption by a single electron readily emerges now by entering $k_{i,f} = \sqrt{2}[E_{i,f} - V_{i,f}(r)]^{1/2}$ (in a.u.) into the expression (3). Note that light absorption implies $E_f > E_i$, while $l \rightarrow l+1$ implies $V_f(r) > V_i(r)$ owing to a larger contribution of centrifugal repulsion in the final state. This combination of circumstances minimizes the value of $k_f(r') - k_i(r')$ in (3), whereas this value would be boosted in the alternative case of $l \rightarrow l-1$ transitions, thus causing (3) to oscillate rapidly and its integral (1) to remain small.
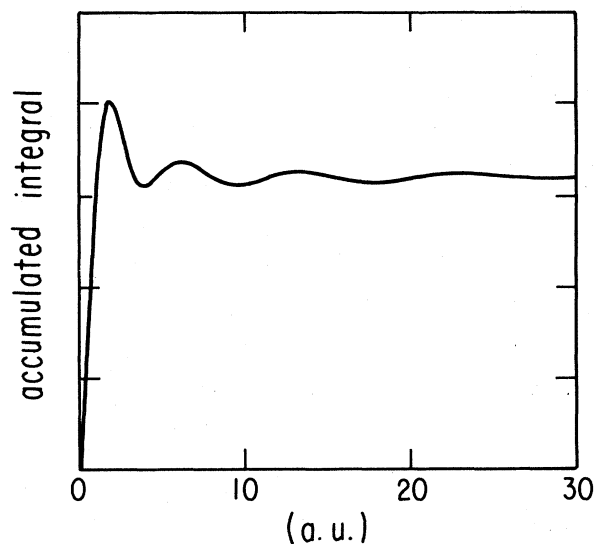
The example outlined above indicates how propensity

FIG. 1. Plot of $\int_0^r f(n=10, \, l=0; r')(r')^{-2} f(\epsilon=0.3, \, l=1; r') \, dr'$ showing rapid rise and rapid oscillatory convergence at radial distances far smaller than the radius ($\sim 10^4$ a.u.) of nonzero overlap between the hydrogenic orbital $f(n=10)$ and the continuum orbital $f(\epsilon=0.3)$ [courtesy of P. Zoller (private communication)].

rules may be traced to the occurrence of a range of stationary phase in the integrand of the relevant matrix element, a range that corresponds to the localization of the rising slope in Fig. 1. A similar analysis also serves to locate the range of the independent variable(s), where a particle may gain a given momentum $k_f(r) - k_i(r)$ from the action of a transition operator $T(r)$, namely, the range where the Fourier representation of $T(r)$ has a large component of frequency $k_f - k_i$. This argument typically restricts the absorption of high-frequency radiation to regions where a particle experiences a strong acceleration.

[1]R. S. Berry, J. Chem. Phys. **45**, 1228 (1966), Sec. IVD.

[2]H. A. Bethe and E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems* (Springer, Berlin, 1957), Sec. 60.2.

[3]See, e.g., U. Fano, Phys. Rev. **135**, B863 (1964); Dan Dill and U. Fano, Phys. Rev. Lett. **29**, 1203 (1972).

[4]Recall that WKB wave functions are often quite accurate; the energy levels are exact for radial functions in a Coulomb field.