

Internal conversion in large molecules

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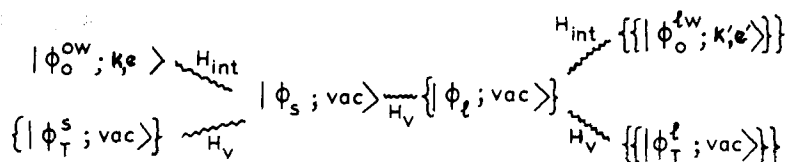
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In this paper we consider the problem of internal conversion in a highly excited singlet state of a large molecule in the statistical limit in terms of a consecutive decay problem. The Wigner-Weisskopf approximation was utilized to handle the problem of sequential decay. We have elucidated the features of the radiative decay, such as the decay pattern, the decay times and the quantum yields of a 'statistical' second-excited singlet state in different spectral regions.

The decaying excited states of large molecules should be described in terms of resonance (or compound) states, similar to the formulations used in the theory of nuclear reactions [1], scattering [2], predissociation and photoionization [3, 4]. A fashionable model for the description of the decaying metastable excited electronic state involves [5] a single zero-order Born-Oppenheimer state ϕ_s which carries oscillator strength from the ground state ϕ_0^0 , coupled to a 'statistical' manifold $\{\phi_l\}$. The $\{\phi_l\}$ dissipative quasicontinuum corresponds to a lower electronic configuration and is inactive in absorption (and emission) in view of spin selection rules (for the case of intersystem crossing), and because of small Franck-Condon factors and propensity rules for intramolecular coupling. In the case of internal conversion from a highly excited singlet state, when the $\{\phi_l\}$ states are electronically excited singlets, they do carry oscillator strength to highly excited vibrational levels ϕ_0^{lw} of the ground electronic state. In view of the symmetry restrictions [6] on the vibrational part of $\{\phi_l\}$ (which has to contain a promoting mode), each of the final ϕ_0^{lw} states has to be characterized by the same vibrational symmetry as the corresponding ϕ_l excited state. Internal conversion from highly excited singlet states in the statistical limit thus corresponds to a consecutive (sequential) decay scheme. Such a physical situation involving a decay of a metastable state (or particle) into another metastable state which subsequently will decay, is encountered in many fields of physics. A common case involves radioactive sequential decay and the decay of elementary particles (for example, a π^+ meson decaying into a μ^+ meson and a neutrino, the former decaying into a positron and two neutrinos [2]). In the present paper we provide a theoretical description of internal conversion in the statistical limit as a sequential decay process, utilizing the Wigner-Weisskopf approximation. The Wigner-Weisskopf scheme is equivalent to the Green's function method [2] provided that (radiative and non-radiative) level shifts are neglected. The Green's function method, previously utilized to provide an incomplete solution to this problem [7] is surveyed in the Appendix, which follows the treatment of Goldberger and Watson [2] for sequential decay of elementary particles.

The total hamiltonian for the system $H = H_{\text{BO}} + H_v + H_R + H_{\text{int}}$ consists of the Born–Oppenheimer hamiltonian, H_{BO} , the intramolecular perturbation, H_v , the radiation field hamiltonian, H_R , and the radiation-matter interaction term H_{int} . The states of H_R will be denoted by $|\text{vac}\rangle$ (the ‘empty’ electromagnetic field) and by $|\mathbf{k}, \mathbf{e}\rangle$ (a single photon characterized by the energy $\hbar|\mathbf{k}|$ and polarization \mathbf{e}). The coupling scheme of the (initially produced) non-stationary state $|\phi_s; \text{vac}\rangle$ corresponding to the second excited singlet is†



where ϕ_0^{ow} are totally symmetric vibronic components of the ground electronic state, ϕ_T^{S} and ϕ_T^{l} correspond to lower triplet manifolds (and the ground state manifold) which can be considered a statistical dissipative quascontinuum and provide additional decay channels for the zero-order states ϕ_s and $\{\phi_l\}$, respectively. The relevant radiative widths are

$$\Gamma_s = 2\pi \sum_{\mathbf{e}} \sum_w \int |\langle \phi_s; \text{vac} | H_{\text{int}} | \phi_0^{\text{ow}}; \mathbf{k}, \mathbf{e} \rangle|^2 \rho_{\mathbf{k}} d\Omega_{\mathbf{k}} \quad (1a)$$

for the state ϕ_s , and

$$\Gamma_l = 2\pi \sum_{\mathbf{e}} \sum_w \int |\langle \phi_l; \text{vac} | H_{\text{int}} | \phi_0^{\text{lw}}; \mathbf{k}', \mathbf{e}' \rangle|^2 \rho_{\mathbf{k}'} d\Omega_{\mathbf{k}'} \quad (1b)$$

for each of the ϕ_l states where $\rho_{\mathbf{k}}$ is the density of states in the radiation field. The pertinent non-radiative (partial) widths for the non-radiative decay of ϕ_s into $\{\phi_T^{\text{S}}\}$ and of each ϕ_l into $\{\phi_T^{\text{l}}\}$ are

$$\Delta_s = 2\pi |\langle \phi_s; \text{vac} | H_v | \phi_T^{\text{S}}; \text{vac} \rangle|^2 \rho_{T^{\text{S}}} \quad (2a)$$

and

$$\Delta_l = 2\pi |\langle \phi_l; \text{vac} | H_v | \phi_T^{\text{l}}; \text{vac} \rangle|^2 \rho_{T^{\text{l}}} \quad (2b)$$

for the state ϕ_s (2a), and for each of the states ϕ_l (2b). Note that on the basis of symmetry arguments we have asserted [6] that the non-radiative decay matrix (in the Born–Oppenheimer representation) is diagonal.

Following conventional time dependent perturbation theory the compound state of the decaying system at time t can be represented in the general form

$$\begin{aligned} \psi(t) = & C_s(t) |\phi_s; \text{vac}\rangle + \sum_l C_l(t) |\phi_l; \text{vac}\rangle + \sum_l \sum_T C_{Tl}(t) |\phi_T^{\text{l}}; \text{vac}\rangle \\ & + \sum_T C_{Ts}(t) |\phi_T^{\text{S}}; \text{vac}\rangle + \sum_{\mathbf{k}\mathbf{e}} \sum_w C_{0w\mathbf{k}\mathbf{e}}(t) |\phi_0^w; \mathbf{k}, \mathbf{e}\rangle \\ & + \sum_{\mathbf{k}\mathbf{e}} \sum_w \sum_l C_{0lw\mathbf{k}\mathbf{e}} |\phi_0^{\text{lw}}; \mathbf{k}, \mathbf{e}\rangle. \end{aligned} \quad (3)$$

The first two terms in equation (3) represent the time evolution of the zero-order

† This physical model has been applied by us previously to the study of the decay of an excited state which is separated by a small energy gap from a lower lying electronic state [6].

vibronic levels corresponding to the second and to the first singlet the third and fourth terms represent the coupling of those vibronic components to the lower triplets (and the ground state), while the last two terms correspond to the radiative decay of the ϕ_s state and of the $\{\phi_l\}$ manifold.

We shall now extend the Wigner-Weisskopf approximation to handle the sequential decay. Adopting the treatment of Bixon *et al.* [8], the contribution of the amplitudes of the final dissipative states $|\phi_T^S; \text{vac}\rangle$, $|\phi_T^I; \text{vac}\rangle$, $|\phi_0^w; \mathbf{k}, \mathbf{e}\rangle$ and $|\phi_0^{lw}; \mathbf{k}, \mathbf{e}\rangle$ can be eliminated and recast in terms of a complex energy contribution. The equations of motion for the vector coefficient $\mathbf{C}(t) = C_s(t)$, $\{C_l(t)\}$ are displayed in the form [6]

$$i \frac{d}{dt} \mathbf{C}(t) = \left(\mathbf{H}_{\text{BO}} + \mathbf{H}_v - \frac{i}{2} \mathbf{\Gamma} - \frac{i}{2} \mathbf{\Delta} \right) \mathbf{C}(t) \quad (4)$$

where $\mathbf{\Gamma}$ is the (diagonal) radiative damping matrix, while $\mathbf{\Delta}$ represents the (diagonal) non-radiative damping matrix. Displaying the expansion coefficients in the interaction representation $\alpha_j(t) = C_j(t) \exp(iE_j t)$ the equations of motion (4) take the form

$$\dot{\alpha}_s = -i \sum_l V_{sl} \alpha_l \exp(iE_s, l t) - \frac{1}{2}(\Gamma_s + \Delta_s) \alpha_s, \quad (5)$$

$$\dot{\alpha}_l = -i \sum_s V_{sl} \alpha_s \exp(-iE_s, l t) - \frac{1}{2}(\Gamma_l + \Delta_l) \alpha_l, \quad (6)$$

where $V_{sl} = \langle \phi_s | H_v | \phi_l \rangle$, and where $E_s, l = E_s - E_l$ represents the difference between the zero-order levels. As the manifold $\{\phi_l\}$ is taken to be quasicontinuous we can now replace the summation over the states of this manifold by an integration, i.e.

$$\sum_l \rightarrow \int dE_l \rho_l, \quad (7)$$

where ρ_l is the density of states in this manifold. We can now also define the non-radiative width Δ_{sl} due to the non-radiative decay of ϕ_s into $\{\phi_l\}$ in the conventional form

$$\Delta_{sl} = 2\pi |V_{sl}|^2 \rho_l, \quad (8)$$

and assume that this width is a slowly varying function of the energy around $E = E_s$.

Now if we substitute the new variables $\beta_s(t)$ and $\{\beta_l(t)\}$ defined by the relations

$$\alpha_s(t) = \beta_s(t) \exp\left(\frac{1}{2} - \gamma_s t\right), \quad (9)$$

$$\alpha_l(t) = \beta_l(t) \exp\left(-\frac{1}{2} \gamma_l t\right), \quad (10)$$

where the total widths of the (zero-order) states are $\gamma_s = \Gamma_s + \Delta_s$ and $\gamma_l = \Gamma_l + \Delta_l$, we get

$$\dot{\beta}_s = -i \sum_l V_{sl} \beta_l \exp\left[-\frac{1}{2}(\gamma_l - \gamma_s)t + iE_s, l t\right], \quad (11 a)$$

$$\dot{\beta}_l = -i V_{sl} \beta_s \exp\left[-\frac{1}{2}(\gamma_s - \gamma_l)t - iE_s, l t\right]. \quad (11 b)$$

Integrating equation (11 b), we get

$$\beta_l(t) = -i V_{ls} \int_0^t \exp\left[-\frac{1}{2}(\gamma_s - \gamma_l)t' - iE_s, l t'\right] \beta_s(t') dt'. \quad (12)$$

The lower bound is taken to be zero in view of the initial conditions imposed on β_l .

Equation (11 *a*) now takes the form

$$\dot{\beta}_s = - \sum_l |V_{sl}|^2 \int_0^t \beta_s(t') \exp \left[-\frac{\gamma_s - \gamma_l}{2} (t' - t) - iE_{s,l}(t' - t) \right] dt'. \quad (13 \ a)$$

Now we shall assume that the widths γ_l are slowly varying functions of the state index and invoking the same assumption concerning the width Δ_{sl} (equation (9)), we get

$$\dot{\beta}_s(t) = -\frac{1}{2}\Delta_{s,l}\beta_s(t), \quad (13 \ b)$$

so that

$$\beta_s(t) = \exp(-\frac{1}{2}\Delta_{s,l}t) \quad (14 \ a)$$

and

$$\alpha_s(t) = \exp(-\frac{1}{2}\tilde{\gamma}_s t) \quad (14 \ b)$$

where the total width of the ϕ_s state is now

$$\tilde{\gamma}_s = \gamma_s + \Delta_{s,l} = \Gamma_s + \Delta_s + \Delta_{s,l}. \quad (15)$$

Inserting (14 *a*) into equation (13 *a*) we get

$$\beta_l(t) = iV_{ls} \frac{\exp[-iE_{s,l}t - \frac{1}{2}(\tilde{\gamma}_s - \gamma_l)t] - 1}{iE_{s,l} + \frac{1}{2}(\tilde{\gamma}_s - \gamma_l)}, \quad (16)$$

so that

$$\alpha_l(t) = iV_{ls} \frac{\exp[-iE_{s,l}t - \frac{1}{2}\tilde{\gamma}_s t] - \exp[-\frac{1}{2}(\Gamma_l + \Delta_l)t]}{iE_{s,l} + \frac{1}{2}(\tilde{\gamma}_s - \Gamma_l - \Delta_l)}. \quad (17)$$

From these results we finally obtain

$$|C_s(t)|^2 = \exp(-\tilde{\gamma}_s t), \quad (18)$$

$$|C_l(t)|^2 = \frac{|V_{sl}|^2}{E_{s,l}^2 + [\frac{1}{2}(\tilde{\gamma}_s - \Gamma_l - \Delta_l)]^2} \{ \exp(-\tilde{\gamma}_s t) + \exp[-(\Gamma_l + \Delta_l)t] - 2\text{Re} \exp[-iE_{s,l}t - \frac{1}{2}(\Gamma_l + \Delta_l + \tilde{\gamma}_s)t] \}. \quad (19)$$

Turning now to an experimental situation, the decay of the system is followed by monitoring the fluorescence in different spectral regions. The differential photon counting rate $\dot{P}(t) = dP/dt$ (over the whole energy region) is

$$\dot{P}(t) = \frac{d}{dt} \left[\int d\Omega_k \sum_{\mathbf{e}} \sum_w |\langle \psi(t) | \phi_0^{0w}; \mathbf{k}, \mathbf{e} \rangle|^2 + \int d\Omega_k \sum_{\mathbf{e}} \sum_w |\langle \psi(t) | \phi_0^{lw}; \mathbf{k}, \mathbf{e} \rangle|^2 \right]. \quad (20)$$

We have previously demonstrated [6] that this expression takes the form

$$\dot{P}(t) = \Gamma_s |C_s(t)|^2 + \sum_l \Gamma_l |C_l(t)|^2. \quad (21)$$

Equation (21) consists of two contributions corresponding to radiative decay channels of different zero-order states. The first term in equations (20) and (21) corresponds to the $\phi_s \rightarrow \phi_0^{0w}$ emission (the *s* region) while the second term represents the $\{\phi_l\} \rightarrow \{\phi_0^{lw}\}$ radiative decay (the *l* region). In the statistical limit we can safely assert that the *s* and *l* regions are well separated in energy. The differential photon

counting in the s region is

$$\dot{P}_s(t) = \Gamma_s |C_s(t)|^2 = \Gamma_s \exp(-\tilde{\gamma}_s t) \quad (22)$$

while in the l region we have for the differential photon counting rate

$$\begin{aligned} \dot{P}_l(t) = \sum_l \Gamma_l |C_l(t)|^2 = \sum_l \frac{\Gamma_l |V_{sl}|^2}{(E_{s,l})^2 + \frac{1}{4}(\tilde{\gamma}_s - \Gamma_l - \Delta_l)^2} \\ \times \{ \exp(-\tilde{\gamma}_s t) + \exp[-(\Gamma_l + \Delta_l)t] \\ - 2 \operatorname{Re} \exp[iE_{s,l}t - \frac{1}{2}(\Gamma_l + \Delta_l + \tilde{\gamma}_s)t] \}. \end{aligned} \quad (23)$$

Invoking the simplifying assumption that the widths Γ_l and Δ_l are constant for all l , and making use of equation (8) the last expression reduces to the form

$$\dot{P}_l(t) = \frac{\Gamma_l \Delta_{s,l}}{\tilde{\gamma}_s - \Gamma_l - \Delta_l} \{ \exp[-(\Gamma_l + \Delta_l)t] - \exp(-\tilde{\gamma}_s t) \}. \quad (24)$$

From these results we conclude that:

(a) The statistical limit for internal conversion can be considered as a simultaneous consecutive decay scheme, whereupon the zero-order state ϕ_s decays radiatively and non-radiatively and can also decay into a $\{\phi_l\}$ continuum, which in turn exhibits again simultaneous radiative and non-radiative decay.

(b) The contribution of the $|C_s(t)|^2$ term to the radiative decay will be exhibited in the energy region close to the electronic origin (0-0) band of the S_2 - S_0 transition. This radiative decay will be exponential and characterized by a lifetime $(\Gamma_s + \Delta_s + \Delta_{s,l})^{-1}$, so that the coupling with the quasicontinuum provides an additional decay channel and an additional width $\Delta_{s,l}$ to the decay of the ϕ_s zero-order state. The quantum yield for emission in this energy region will be

$$Y_s = \frac{\Gamma_s}{\Gamma_s + \Delta_s + \Delta_{s,l}}. \quad (25)$$

These results are not surprising as they just correspond to the decay of a single resonance in the statistical limit.

(c) The second contribution $\dot{P}_l(t)$ to the radiative decay will occur to highly vibrationally excited states of the ground state, and will be exhibited in the spectral region close to the S_1 - S_0 transition. This decay pattern will exhibit a short-time behaviour of the form $\dot{P}_l(t \rightarrow 0) = \Gamma_l \Delta_{s,l} t$ and a long-time behaviour $\dot{P}_l(t) \propto \exp[-(\Gamma_l + \Delta_l)t]$. The long-time decay pattern in this energy range corresponds to the decay from the lowest excited singlet. The quantum yield for the radiative decay in this spectral region will be

$$Y_l = \frac{\Gamma_l \Delta_{s,l}}{\tilde{\gamma}_s (\Gamma_l + \Delta_l)}. \quad (26)$$

(d) The experimental decay times in the two well separated spectral regions where the ϕ_s state and where the $\{\phi_l\}$ manifold contribute to the radiative decay will be appreciably different, being $\tilde{\gamma}_s^{-1}$ in the 'high' energy range and $(\Gamma_l + \Delta_l)^{-1}$ in the 'low' frequency region. Thus, the emission spectrum is constituted of a high energy short lifetime range and a low energy long lifetime region.

(e) The total yield for emission is given by

$$Y = Y_s + Y_l = \frac{\Gamma_s}{\tilde{\gamma}_s} + \frac{\Gamma_l \Delta_{sl}}{\tilde{\gamma}_s(\Gamma_l + \Delta_l)} \quad (27)$$

while the ratio of the fluorescence quantum yields in the 'low' and 'high' frequency regions is

$$R = \frac{Y_l}{Y_s} = \frac{\Gamma_l \Delta_{s,l}}{\Gamma_s(\Gamma_l + \Delta_l)}.$$

(f) As we have assumed, the radiative and non-radiative decay patterns of each of the zero-order states are independent, thus the physical situation in the statistical limit for internal conversion is, in fact, satisfactorily represented by conventional kinetic expressions. Thus, equation (22) represents a conventional kinetic formula for the parallel decay of the zero-order states into three decay channels, while equation (24) represents a consecutive classical decay scheme, where states in the $\{\phi_l\}$ manifold are populated by the decay of the ϕ_s levels and then can decay by two parallel radiative and non-radiative channels.

(g) Interference effects in the radiative decay will not be exhibited and quantum beats will not be observed in the statistical limit for internal conversion. The situation is analogous to the decay of a single resonance.

APPENDIX

Consecutive decay by the Green's function method

We shall present a treatment of consecutive decay using the Green's function method, following very closely the general techniques developed by Goldberger and Watson [2]. Consider a simplified model system where an initial state $|s\rangle$ is coupled to a quasicontinuum $\{|l\rangle\}$, while each of the states $|l\rangle$ decays into a quasicontinuum $\{|j\rangle\}$. We should note in passing that on the basis of physical arguments we can assert that, in fact, each of the $|l\rangle$ levels decays into its own quasicontinuum $\{|jl\rangle\}$ and interference effects can be disregarded. However, in what follows, we can replace the double index jl by a single index j . Let us denote the operator which couples $|s\rangle$ and $\{|l\rangle\}$ by V_1 , while the operator which induces the consecutive decay step, by V_2 . For the case of internal conversion from the second excited singlet state, $V_1 = H_v$, while $V_2 = H_{\text{int}}$. We should also note that these two coupling operators may originate from the same physical perturbation (say H_v). Such a physical situation may be encountered for the decay of the first excited singlet state into the second triplet, which in turn decays into the first triplet manifold. In this case we shall utilize the following projection operators:

$$P_s = |s\rangle\langle s|, \quad Q = \sum_l |l\rangle\langle l| = \sum_l P_l$$

and

$$O = \sum_j |j\rangle\langle j| = \sum_j P_j,$$

in terms of which we define

$$V_1 = PH_vQ + QH_vP, \quad (\text{A } 1)$$

$$V_2 = QH_vO + OH_vQ, \quad (\text{A } 2)$$

where we have made use of the assumption that the initial state $|s\rangle$ is not coupled directly to the final continuum $\{|j\rangle\}$.

The pertinent matrix elements of the Green's operator are [2]

$$\langle s|G(E)|s\rangle = \frac{1}{E - E_s - R_{ss}^S(E)}, \quad (\text{A } 3)$$

$$\langle l|G(E)|l\rangle = \frac{1}{E - E_l - R_{ll}^L(E)}, \quad (\text{A } 4)$$

$$\langle l|G(E)|s\rangle = \frac{1}{E - E_l - R_{ll}^L(E)} R_{ls}^S(E) \frac{1}{E - E_s - R_{ss}^S(E)}, \quad (\text{A } 5)$$

where $R_{ab}^I = \langle a|R^I|b\rangle$ and

$$R^S = V_1 + V_1(1 - P_s) \frac{1}{E - H_0 - (1 - P_s)V_1(1 - P_s)} (1 - P_s)V_1 \quad (\text{A } 6)$$

$$R^L = V_2 + V_2(1 - P_l) \frac{1}{E - H_0 - (1 - P_l)V_2(1 - P_l)} (1 - P_l)V_2. \quad (\text{A } 7)$$

In terms of these matrix elements the probability to find the system in the initial state is given by $|C_s(t)|^2$ where

$$C_s(t) = \frac{1}{2\pi i} \int_e dE \exp(-iEt) G_{ss}(E) \quad (\text{A } 8)$$

and the probability for finding the system at time t in the intermediate continuum is

$$\sum_l |C_l(t)|^2$$

where

$$C_l(t) = \frac{1}{2\pi i} \int_e dE \exp(-iEt) G_{ls}(E). \quad (\text{A } 9)$$

e is a contour which goes from infinity to minus infinity above the real axis.

Applying the usual assumptions about the smoothness of the functions $R_{ss}^S(E)$ and $R_{ll}^L(E)$ (as functions of E) one defines [2]

$$R_{ll}^L(E_l) \simeq D_l - i \frac{\Gamma_l}{2}, \quad (\text{A } 10)$$

$$R_{ss}^S(E_s) \simeq D_s - i \frac{\Gamma_s}{2}, \quad (\text{A } 11)$$

where D and Γ are level shifts and widths, respectively. The complex integrations (A 9) and (A 11) may now be performed using the procedure described by Goldberger and Watson [2], the results are (neglecting branch cut contributions)

$$C_s(t) \simeq \exp \left[-i(E_s + D_s)t - \frac{i}{2} \Gamma_s t \right] \quad (\text{A } 12)$$

and

$$C_l(t) \simeq \frac{R_{ls}}{E_l - E_s + D_l - D_s + \frac{i}{2}(\Gamma_s - \Gamma_l)} \times \left\{ 1 - \exp \left\{ i \left[E_l - E_s + D_l - D_s + \frac{i}{2}(\Gamma_s - \Gamma_l) \right] t \right\} \right\}. \quad (\text{A } 13)$$

These results lead to

$$|C_s(t)|^2 = \exp(-\Gamma_s t) \quad (\text{A } 14)$$

and

$$\begin{aligned} \sum_l |C_l(t)|^2 &= \int dE_l \rho(E_l) \frac{|R_{sl}|^2 \exp(-\Gamma_l t)}{(E_l - E_s + D_l - D_s)^2 + \left(\frac{\Gamma_s - \Gamma_l}{2}\right)^2} \\ &\quad \times \left\{ 1 - 2 \exp\left(-\frac{\Gamma_s - \Gamma_l}{2} t\right) \cos[(E_l + D_l - E_s - D_s)t] \right. \\ &\quad \left. + \exp[-(\Gamma_s - \Gamma_l)t] \right\} \\ &= \frac{1}{\Gamma_s - \Gamma_l} (\exp[-\Gamma_l t] - \exp[-\Gamma_s t]) \times 2\pi\rho(E_l) |R_{sl}|^2 \\ &= \frac{\Gamma_s}{\Gamma_s - \Gamma_l} (\exp[-\Gamma_l t] - \exp[-\Gamma_s t]). \end{aligned} \quad (\text{A } 15)$$

Substituting these results in equation (21) we shall of course obtain the final result (equation (24)). [Note that here we have excluded some of the additional decay processes which were included in the Wigner-Weisskopf scheme.]

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