The Einstein A & B coefficients

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- Review of transition probabilities

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- Spontaneous emission coefficient

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The probability of stimulated emission (and absorption) of radiation from a two state system depends on the perturbative Hamiltonian $H' = -\mathcal{P}E_0\cos(\omega t)$, where the polarization is $\vec{\mathcal{P}} = q\langle\psi_b|\vec{r}|\psi_a\rangle$

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While Einstein did not have the benefit of quantum electrodynamics, he was able to calculate the coefficient of spontaneous emission, which cannot be calculated using semi-classical perturbation methods but must be related to stimulated emission. Einstein used what was known about quantum mechanics and experimental evidence to perform this calculation.

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But which transitions are allowed?

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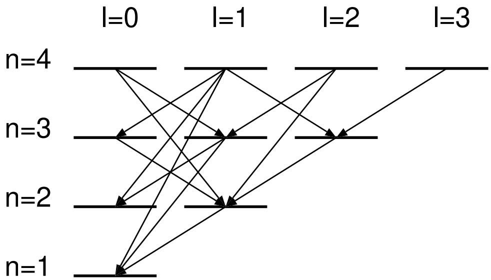

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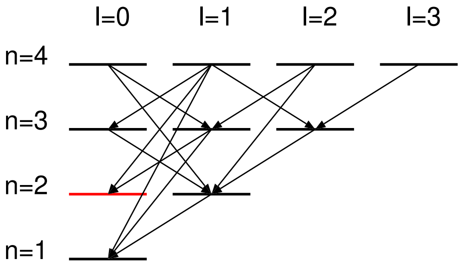

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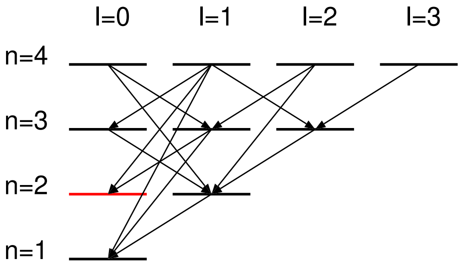

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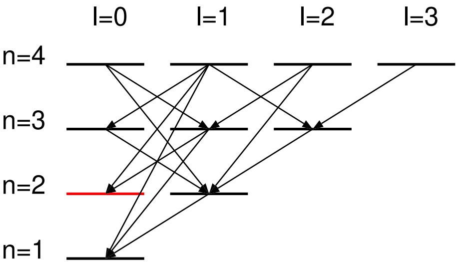

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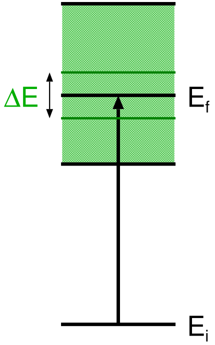
must calculate the transition probability of an initial state of energy E_i making a transition to a state with an energy in a finite range, ΔE about E_f using an integral over the density of possible final states



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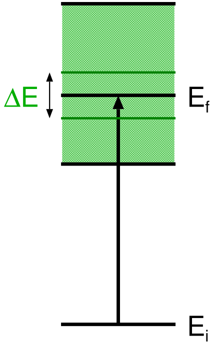

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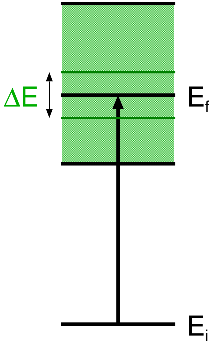

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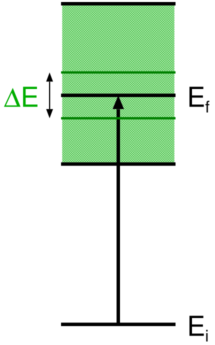

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as with the simple two level model, at long times t, the integrand is sharply peaked about $E_f = E_i + \hbar\omega$

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The probability of transition thus simplifies to

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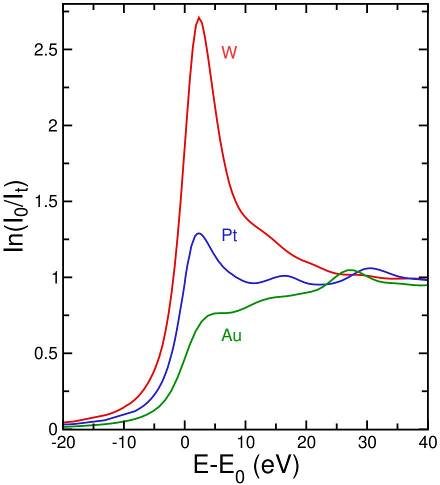

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the transition probability is $\sim \alpha^2$ smaller than the dipole transition probability

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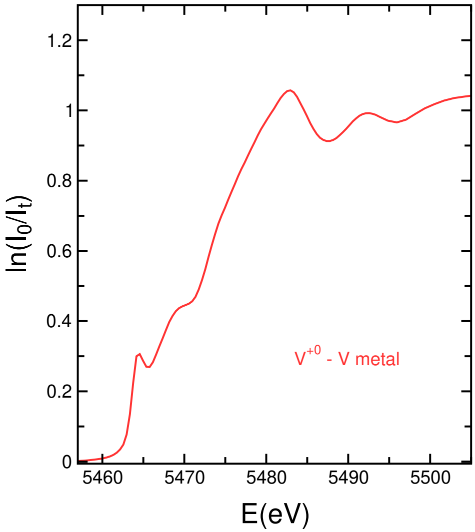

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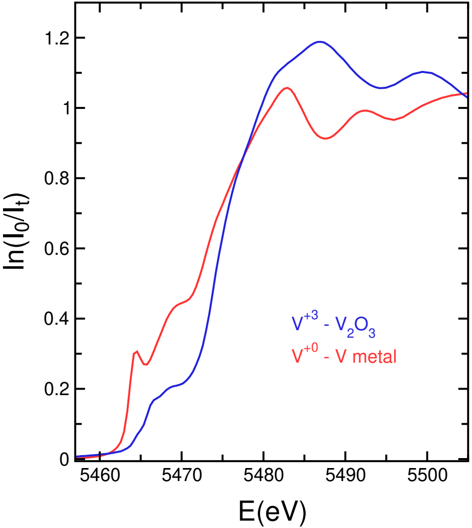

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As the oxidation state of the metal atom increases, the nuclear screening decreases and the ionization energy increases

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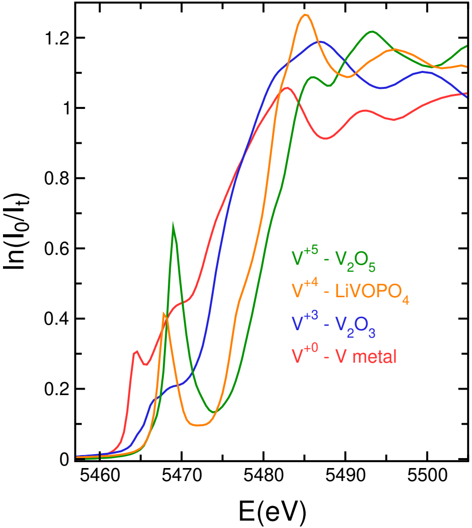

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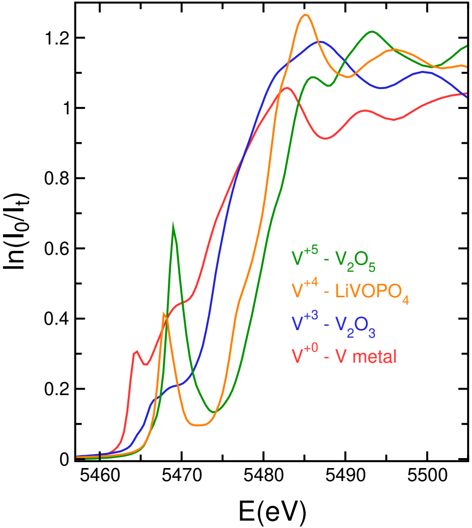

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The size of the pre-edge peaks often correlates with the number of empty d-states as well as the local geometry (crystalline electric fields)