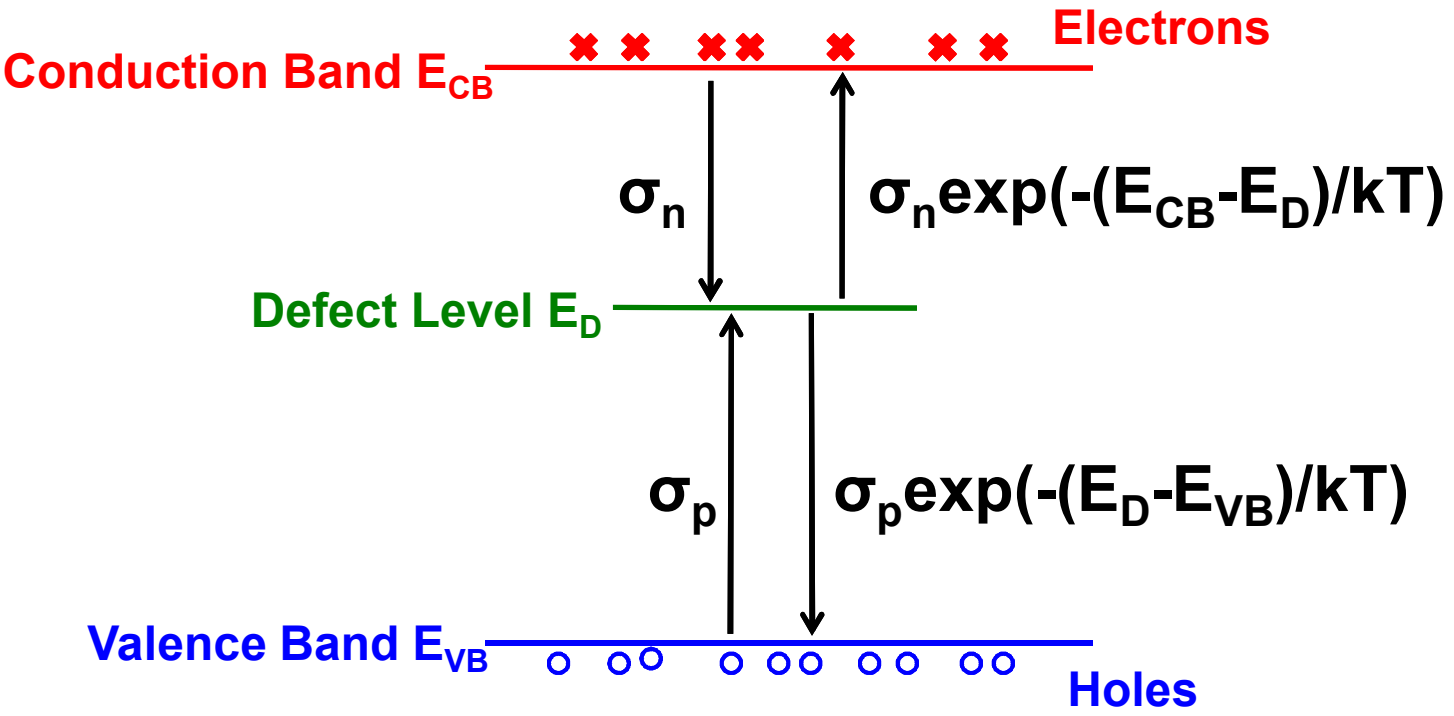
SAND2015-3792C

DFT Calculations of Activation Energies for Carrier Capture by Defects in Semiconductors



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How Much Do Real Cross-Sections Vary?

Henry and Lang, PRB 1977 studied
13 cross-sections in GaAs and GaP

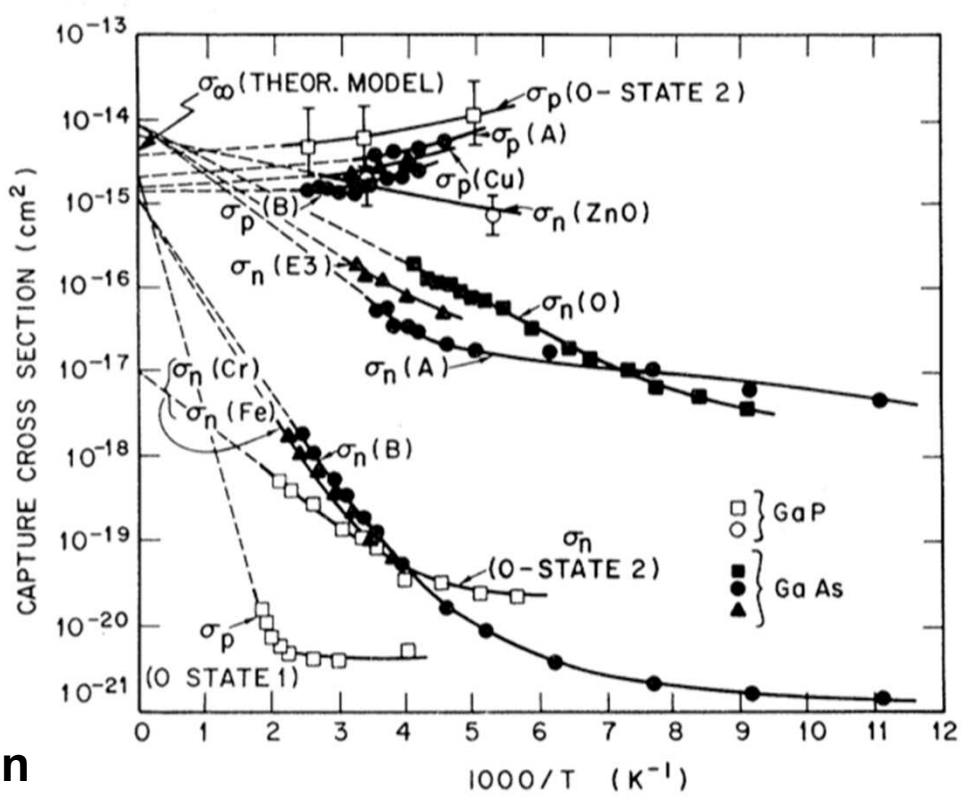
Wide variation at room-temperature

Extrapolate to similar values at high-T

Generally, have the high-T form

$$\sigma(T) = \sigma_\infty \exp(-E_B/kT)$$

Henry and Lang's theory of Multiphonon Emission explains this result



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Henry and Lang Theory of Carrier Capture

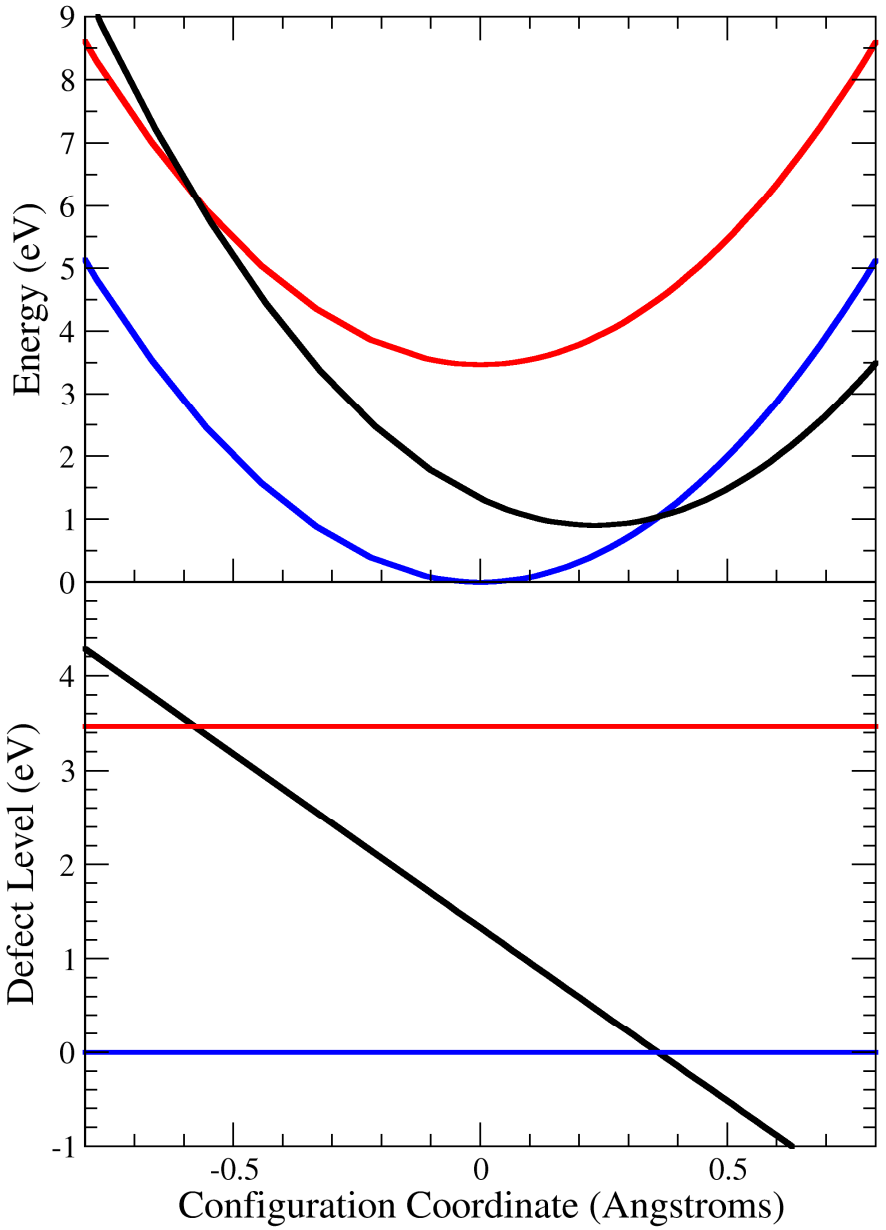
Assume a configuration coordinate λ

Upper Panel: λ-Dependent Energies
Blue Line: Q_D=q with no carriers
Black Line: Q_D=q-1 with a hole
Red Line: Q_D=q with hole and electron

Lower Panel: λ-Dependent Defect Level
Black Line:q-1/q defect level
Blue Line: Valence band
Red line: Conduction band

Nonradiative capture/emission occurs near level crossings when energy can be conserved

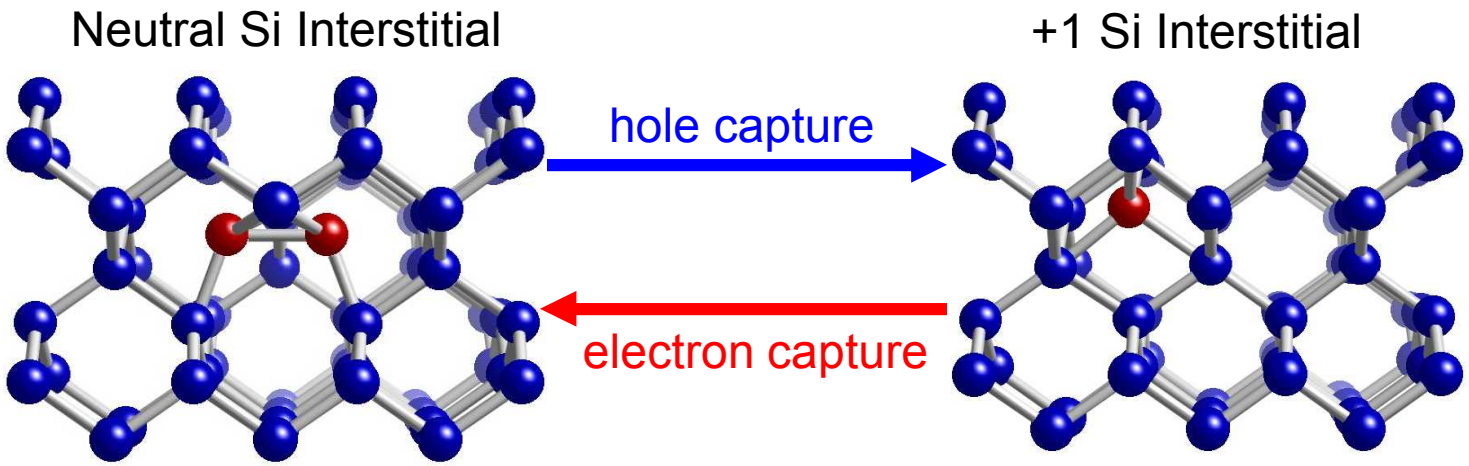
Activation energies given by differences between crossing-points and minima



First-Principles Calculations of Carrier Capture

Detailed theories based on DFT perturbation theory (L. Shi and L.-W. Wang, PRL 2012; A. Alkauskas et al., PRB 2014) have been developed to calculate capture cross-sections when the harmonic approximation holds

Instead, we have considered the anharmonic case:



So far, we have focused on carrier capture activation energies and the high-T behavior

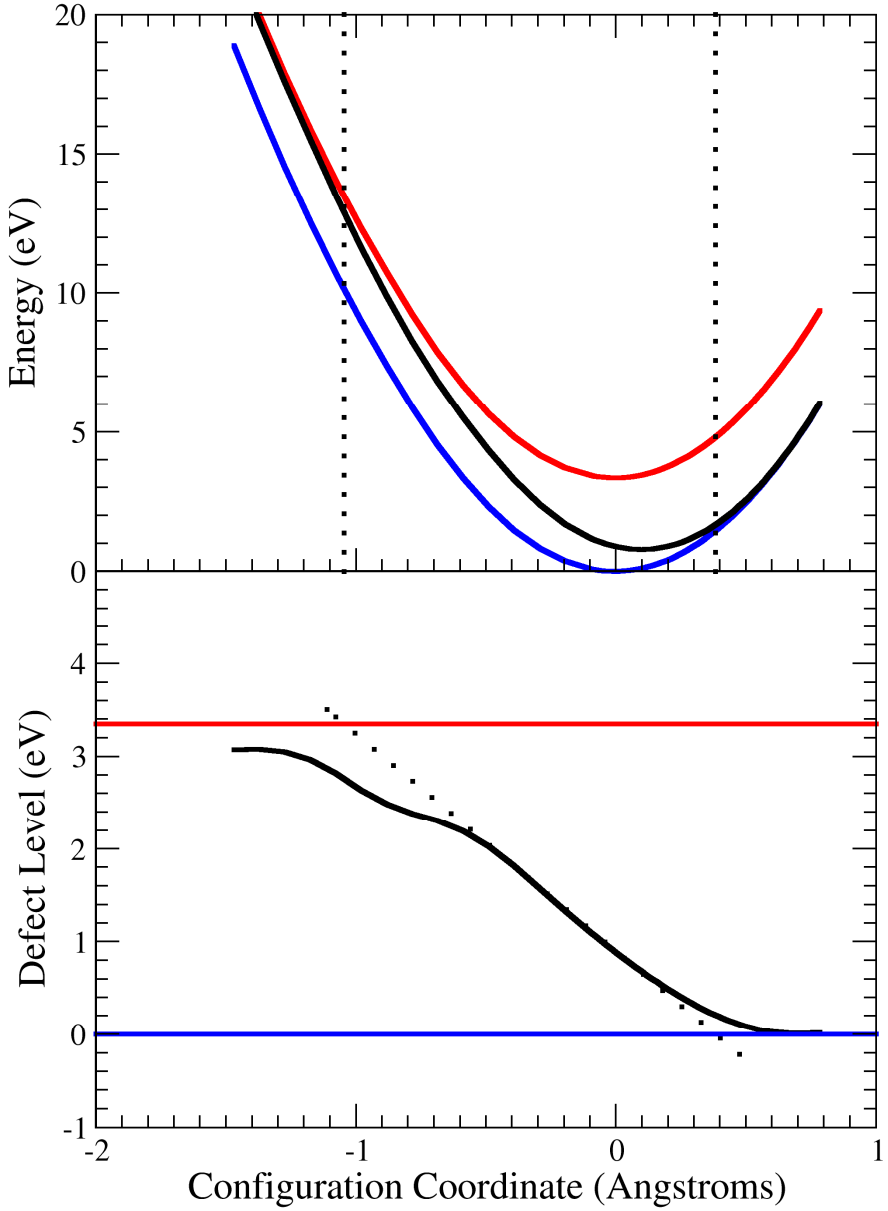
DFT w/ Assumed Configuration Coordinate

V_{Ga} -2/-3 level in GaN – Possibly associated with yellow luminescence

Extrapolated configuration coordinate from difference in relaxed structures

Upper Panel:
Blue Line: Q_D=-2 with no carriers
Black Line: Q_D=-3 with a hole
Red Line: Q_D=-2 with hole and electron

Lower Panel:
Black Line:-3/-2 defect level
Blue Line: Lower Bound
Red line: Upper Bound



Configuration Coordinate Optimization

We have developed a new algorithm inspired by transition state finding methods

For a given defect level, perform a constrained minimization of the defect energy over configurations consistent with that level

As the level is varied, consider the pathway of such configurations

If “diabatic” energies were used, the pathway would pass through the transition states for carrier capture

The minimization is easily accomplished by mixing Newton steps parallel to the force difference vector with perpendicular relaxation steps

DFT w/ Optimized Configuration Coordinate

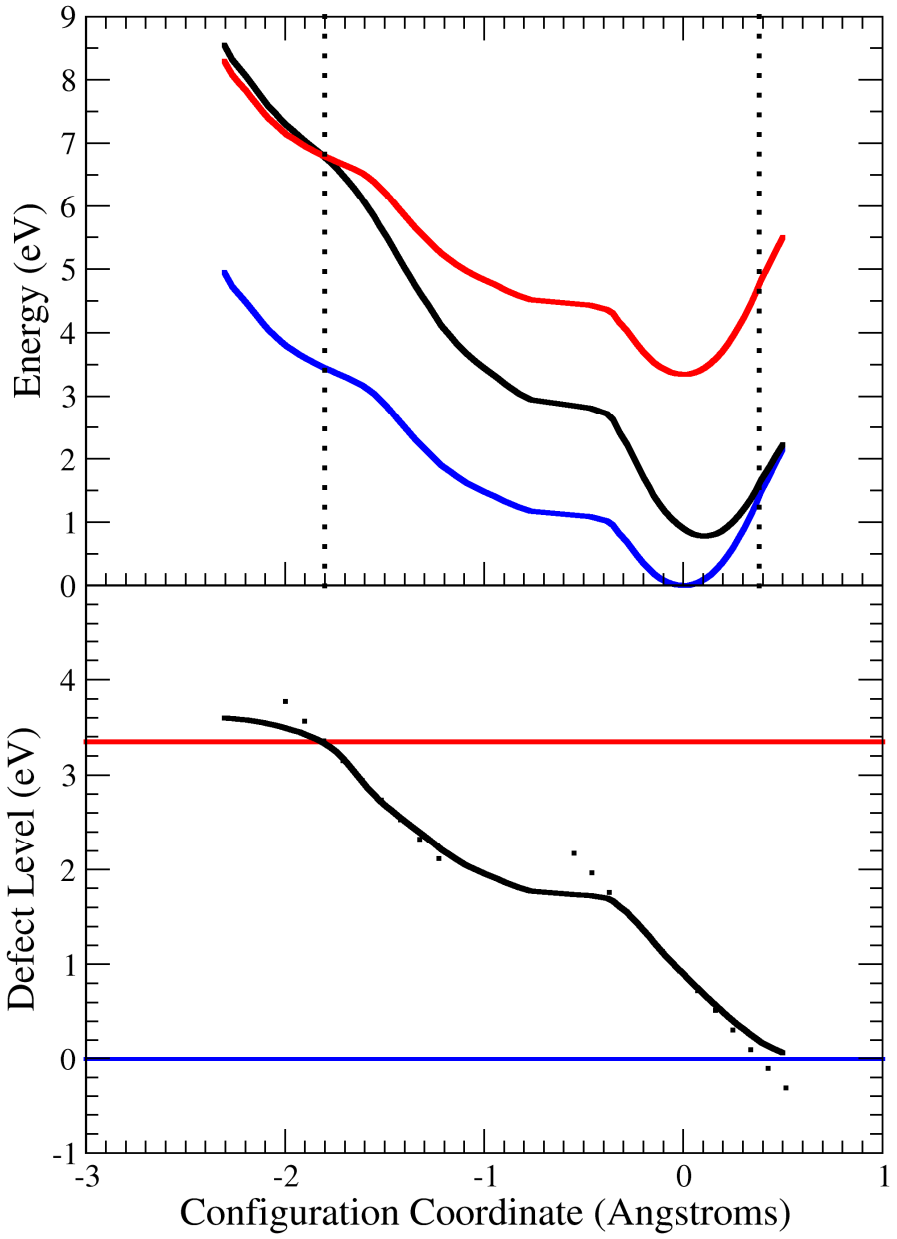
For hole capture, optimization doesn't change the results very much

For electron capture, a complex, symmetry breaking distortion is observed beyond about 0.4 A

Extrapolation Gives:

3.45 eV activation energy for electron capture which is consistent with yellow luminescence – Good!

0.83 eV activation energy for hole capture – Maybe too large?



Next Steps For This Work

Study more defects looking for cases where direct comparison with experiment is possible

Extend our procedures to the full temperature range: S and ω are easily calculated near the ground state configurations, but how do we smoothly patch together our anharmonic, multidimensional results for high temperature with the harmonic theory for low temperatures?

In general, we probably have to solve the anharmonic Schrodinger equation for vibration along the configuration coordinate.

Do These Classical Activation Energies Generally Control the High Temperature Behavior?

Henry and Lang obtained the same result from the high-T limit of the fully quantum expressions in the harmonic case

Quantum and classical results should agree at high-T based on the Correspondence Principle

We have checked two cases carefully:

- Does the classical barrier give the high-T slope for small relaxation energies? YES
- Does the classical barrier give the high-T slope when you consider thermal excitation of the band edge carriers? YES

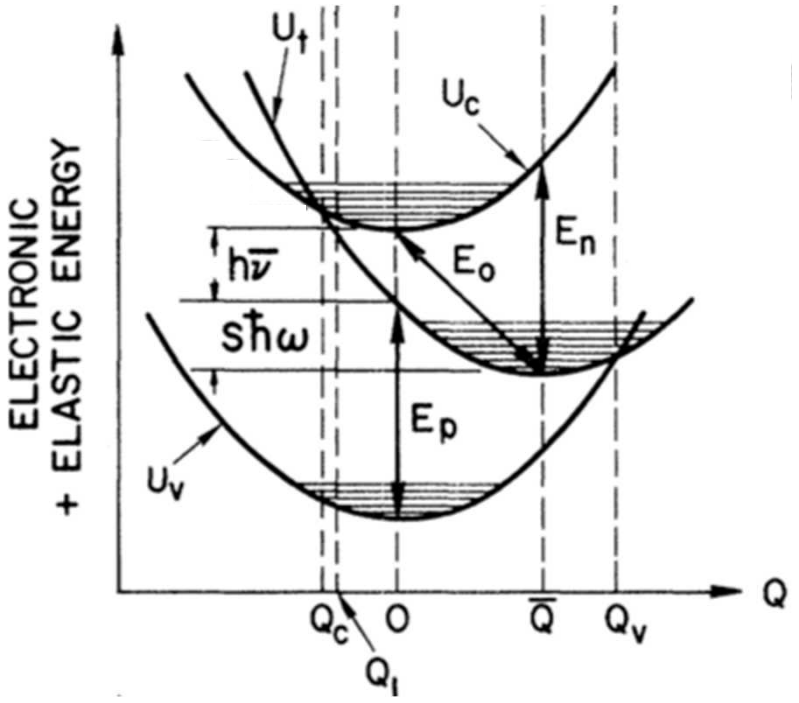
Thanks for help from Audrius Alkauskas and Bill Wampler!

Model for Calculating Capture Cross-Sections

Q is an ionic configuration coordinate

U_v is the energy of neutral system with defect
U_c is the energy with extra electron in CB
U_t is the energy with extra electron on defect

Q=0 is the minimum for neutral defect
$Q=\bar{Q}$ is the minimum for charged defect
U_c and U_t cross at $Q=Q_c$
U_v and U_t cross at $Q=Q_v$



E_p is the optical excitation threshold from VB
E_n is the optical excitation threshold from defect
$h\bar{\nu}$ is the zero-phonon emission line from CB
$S\hbar\omega$ is the relaxation energy for the charged defect
E_0 is the thermodynamic defect level (relative to the CB)

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Model for Calculating Capture Cross-Sections

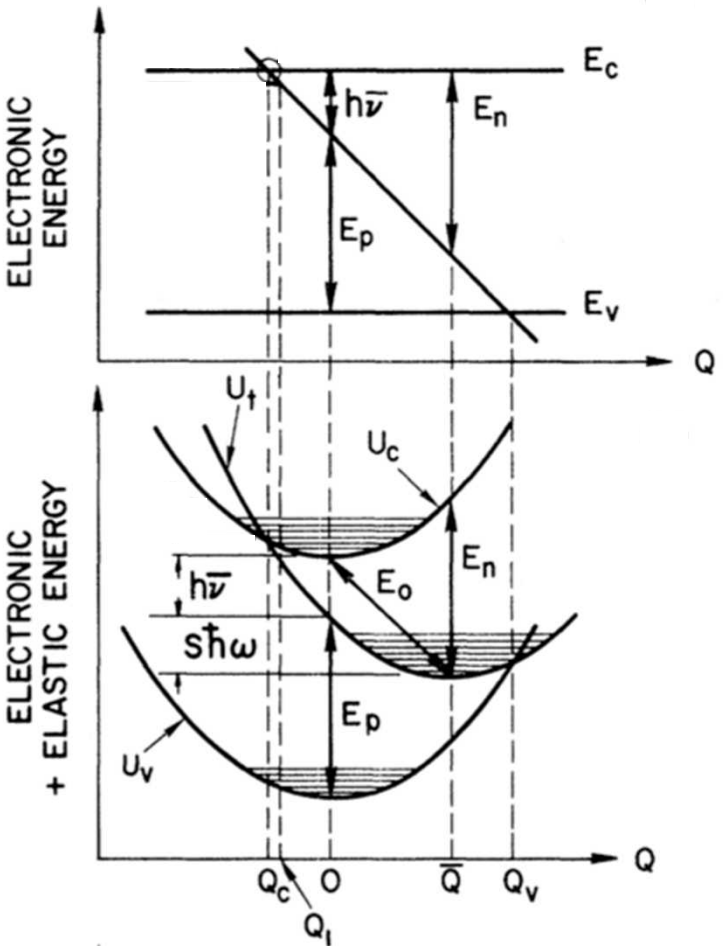
Normally, the defect level is defined as the difference of relaxed charge state energies

Alternatively, we can define a Q dependent defect level for charge states at the same Q

This defect level crosses into the CB at $Q=Q_c$ and the VB at $Q=Q_v$

These level crossing regions dominate the thermal capture and emission of carriers

We can define Q_1 as the point where the adiabatic approximation begins to break down



Q_1 is taken to be 0.06 eV from the crossing in Henry and Lang

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Calculating Nonradiative Capture Cross-sections

Perturbation theory for the transition rate gives

$$w = \frac{2\pi}{\hbar}\,\mathrm{ave}_{n_c}\sum_{n_t}\left|\langle t n_t|\mathcal{H}|c n_c\rangle\right|^2\delta(\mathcal{E}_c-\mathcal{E}_t)$$

Where $|n_c\rangle$ and $|n_t\rangle$ are vibrational states,

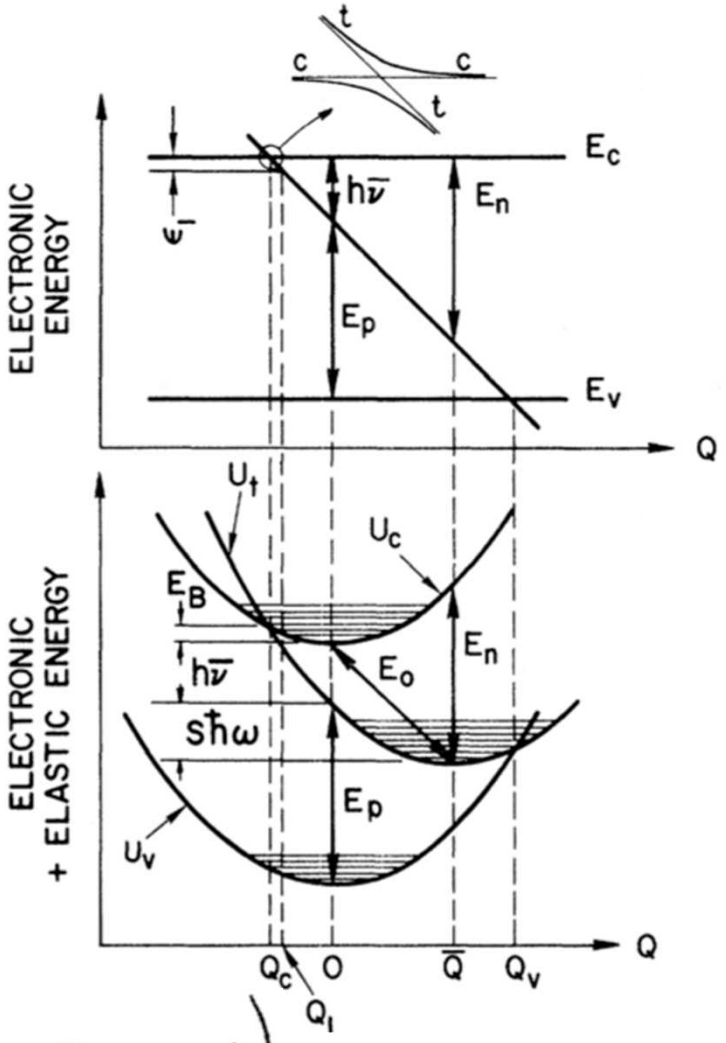
$$\mathcal{E}_c = n_c\hbar\omega\text{, and }\mathcal{E}_t = n_t\hbar\omega - E_0$$

Result is dominated by level crossing region, so assume that $|c\rangle$ and $|t\rangle$ are constant

$$|c\rangle = u_c(r, Q_1),\quad |t\rangle = u_t(r, Q_1)$$

Then, defining $\Delta V(r, Q) = V(r, Q) - V(r, Q_1)$

$$w = \frac{2\pi}{\hbar}\left|\langle t|\Delta V|c\rangle\right|^2\left(\mathrm{ave}_{n_c}\sum_{n_t}\left|\langle n_t|n_c\rangle\right|^2\delta(\mathcal{E}_c-\mathcal{E}_t)\right)$$



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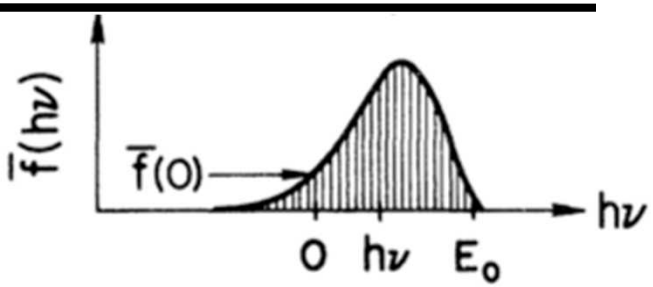
Calculating Nonradiative Capture Cross-sections

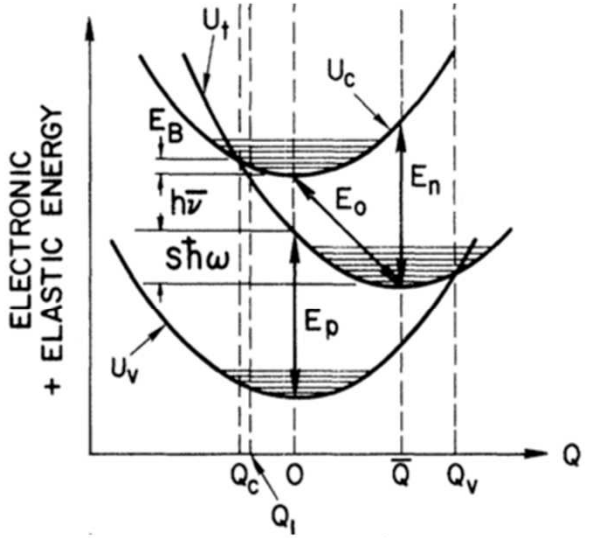
Defining the "Normalized Line Shape"

$$f(h\nu) = \mathrm{ave}_{n_c} \sum_{n_t} |\langle n_t | n_c \rangle|^2 \, \delta(\mathcal{E}_c - \mathcal{E}_t - h\nu)$$



And using $\sigma_c = (\Omega / \langle v \rangle) w$ **, we get**

$$\sigma_c = \underbrace{(2\pi\Omega / \hbar\langle v \rangle) |\langle c | \Delta V | t \rangle|^2}_{\text{Weakly Varying}} \underbrace{f(0)}_{\text{Strongly Varying}}$$



For Radiative Recombination, similar arguments give

$$\frac{dw^{\mathrm{rad}}}{d(h\nu)} = \frac{2\pi}{\hbar} \mathrm{ave}_{n_c} \sum_{n_t} |\langle u_t \, n_t | H_{\mathrm{rad}}(r) | u_c \, n_c \rangle|^2 \, \delta(\mathcal{E}_c - \mathcal{E}_t - h\nu) \rho_{\mathrm{rad}}$$

$$= \frac{2\pi}{\hbar} \rho_{\mathrm{rad}} |\langle \varphi_t | H_{\mathrm{rad}} | \varphi_c \rangle|^2 f(h\nu) \sim (h\nu)^3 f(h\nu)$$

where φ_c **and** φ_t **are evaluated at** $Q = 0$ **(the Condon Approximation)**

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Observations about the Normalized Line Shape

If we assume simple harmonic oscillators with the same frequency, we get the Huang and Rhys line shape, a function of E_0 $\hbar\omega$ **and** S

$$f(h\nu) = \sum_{p=-\infty}^{\infty} \delta(E_0 - p\hbar\omega - h\nu) W_p$$

Where

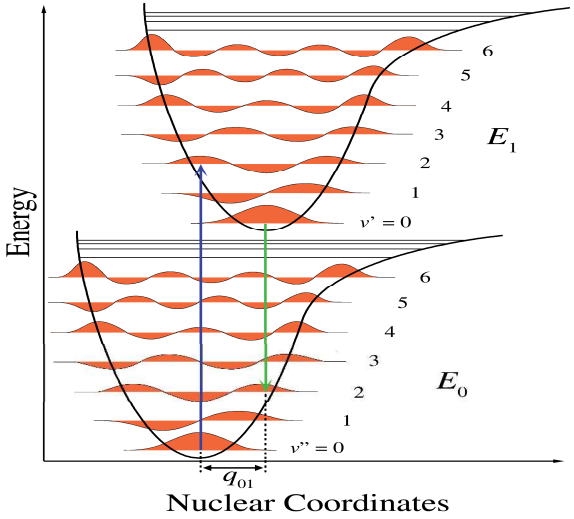
$$W_p = \exp[-(2n+1)S][(\bar{n}+1)/\bar{n}]^{p/2} \times I_p(2S[(\bar{n}+1)\bar{n}]^{1/2})$$

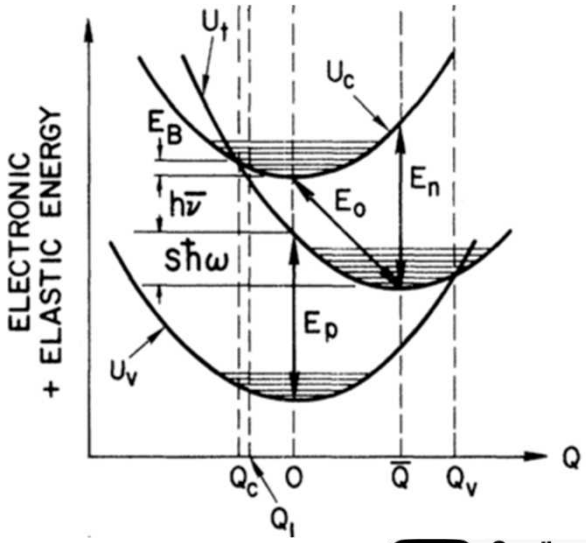
I_p **is a modified Bessel function, and**

$$\bar{n} = [\exp(\hbar\omega/kT) - 1]^{-1}$$

At high temperature, we obtain

$$\sigma_c = \left(\frac{4\pi E_B}{kT}\right)^{1/2} \frac{\Omega |\langle t|\Delta V|c\rangle|^2}{\hbar\langle v\rangle h\bar{\nu}} e^{-E_B/kT}$$





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Comparison of Our Calculated Barriers for V_{Ga} to Experiments on Yellow Luminescence

Experiment suggests electron capture barrier > 0.6 eV

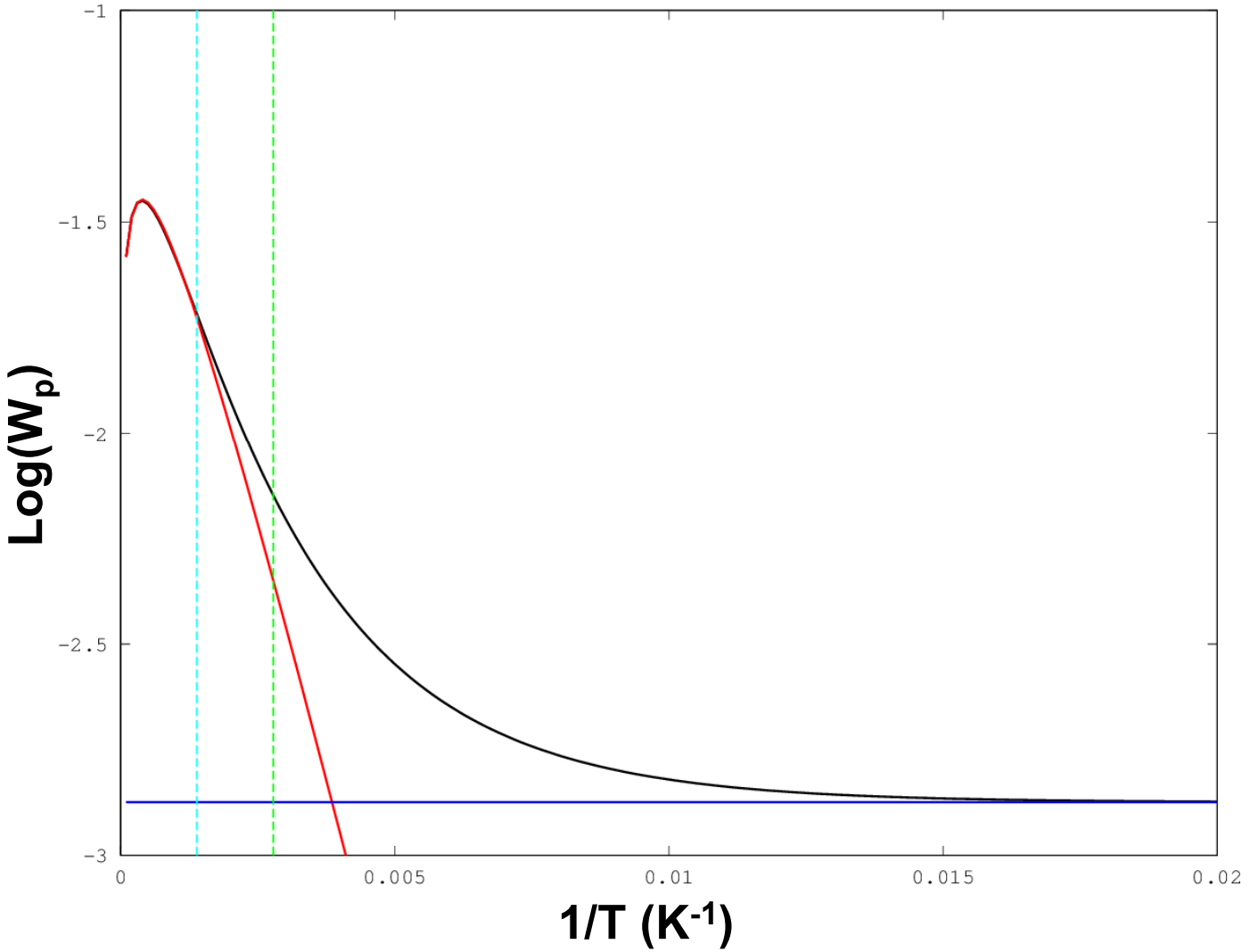
We get 3.45 eV. Good!

However, the hole capture barrier 0.83 eV would suggest that non-radiative capture of holes would be slower than observed

Some possible explanations:
Convergence with respect to supercell size and/or BZ sampling
Better functionals (e.g., hybrids) might be needed
V_{Ga} must be in a defect complex to contribute to YL
Some other defect (e.g., C_N) is solely responsible for YL

Is This High Temperature Limit Generally Valid?

Evaluate exact W_p (Black) and Approximate W_p (Red) including the $T^{-1/2}$ factor for E_0=0.31eV, hω=0.031 eV, and S=3.226



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