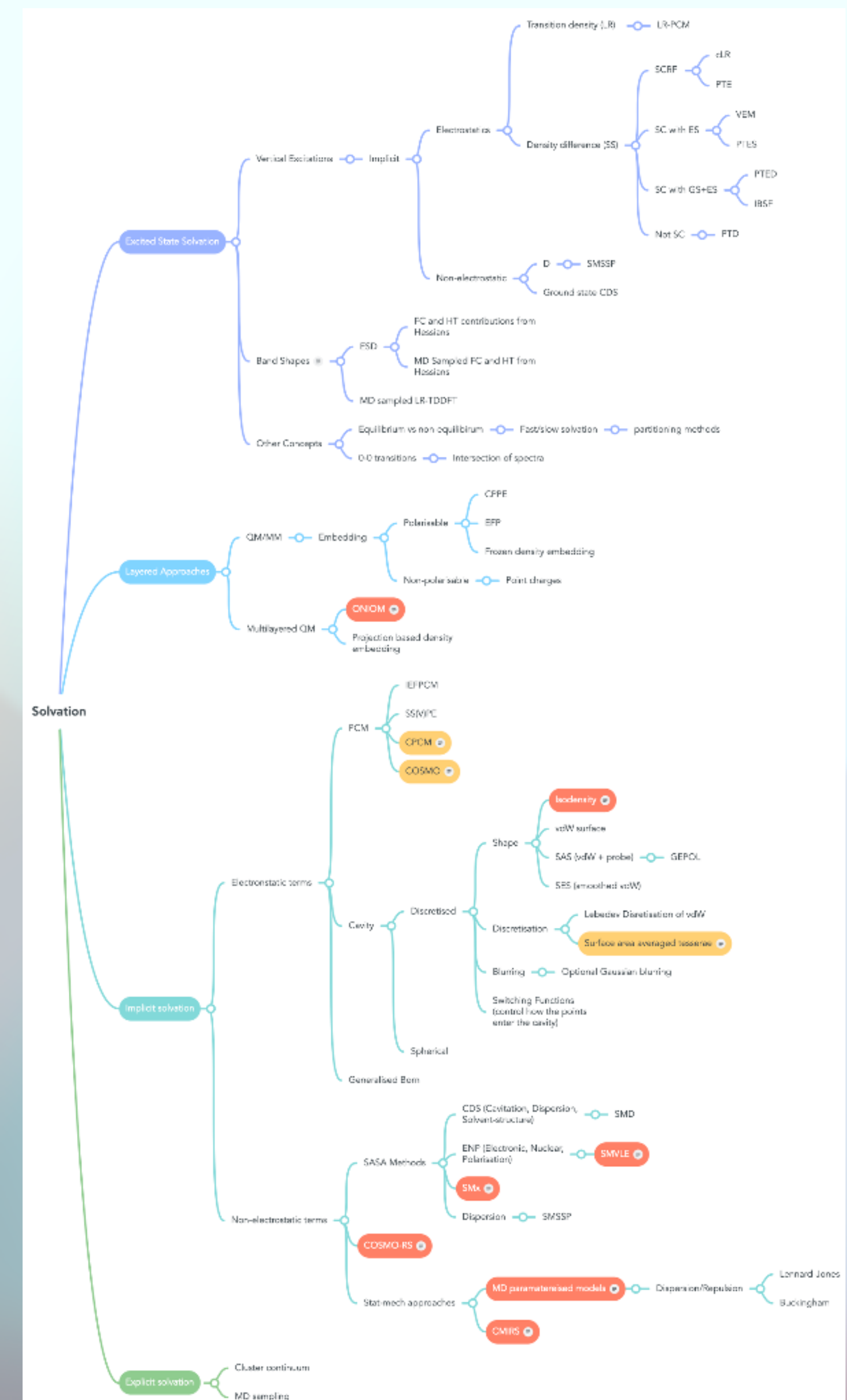


Solvation Models and Excited States

A (hopefully) helpful guide

What this is



Disclaimer

I'm only just starting my PhD, and this field is an absolute mess. It's poorly documented, inconsistently implemented, often black box without specification, and assumes you "just know" already. Most of the proofs and explanations are given in some of the heaviest maths imaginable and it's taken me a solid 8 months just to get to where I am. I chose to make this presentation, because I wish I had a resource like this, and making these slides has reminded of how little I truly understand. These have not been fact checked by a higher authority.

DO NOT hold me responsible if anything in here is wrong.

Solvation models (ground state)

Explicit solvation

- Cluster solvation - only models one structure
- MD Sampling is required
- Lacks long range electrostatics when using a small solvent shell
 - Gets VERY expensive if you don't
- Multilevel approaches lack mutual polarisation
- Density embedding
 - Requires QM calculations for the solvent region
 - Few analytical gradients implemented
- **Energy and properties are solvent-structure dependent**

This is all I will say about explicit solvation...

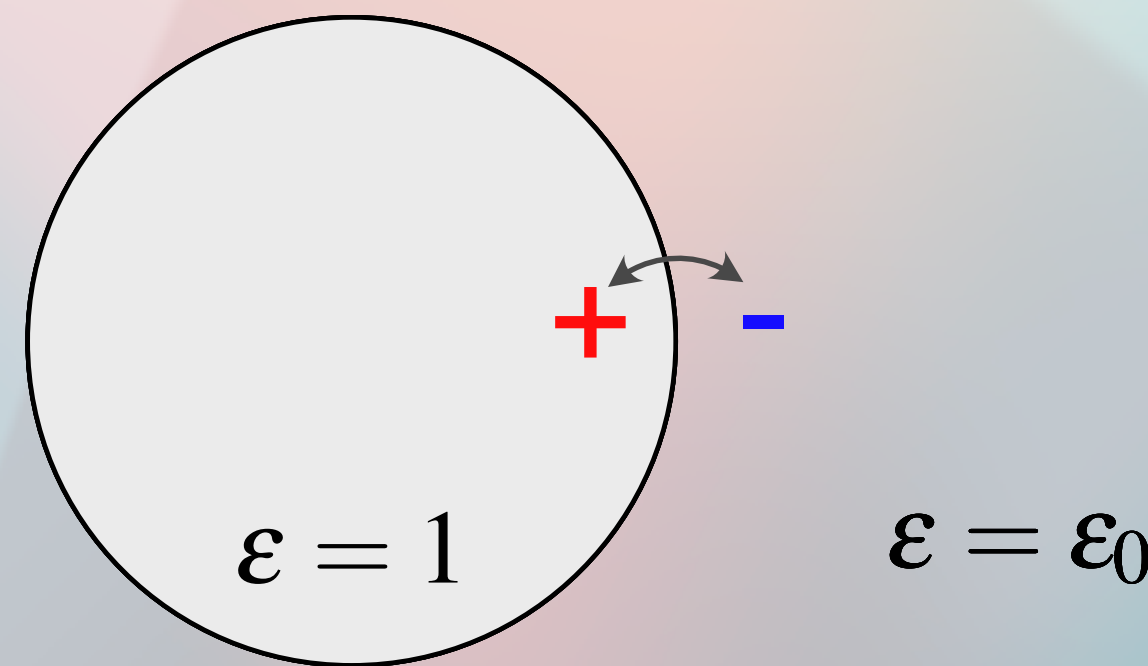
Implicit solvation

$$\Delta G_{solv}^{\circ} = \Delta G_{el}^{\circ} + \Delta G_{cav}^{\circ} + \Delta G_{dis}^{\circ} + \Delta G_{rep}^{\circ} + \Delta G_{solv-struc}^{\circ} + \Delta G_{CT}^{\circ}$$

$$\Delta G_{solv}^{\circ} = \Delta G_{el}^{\circ} + \Delta G_{non-el}^{\circ}$$

Electrostatic terms

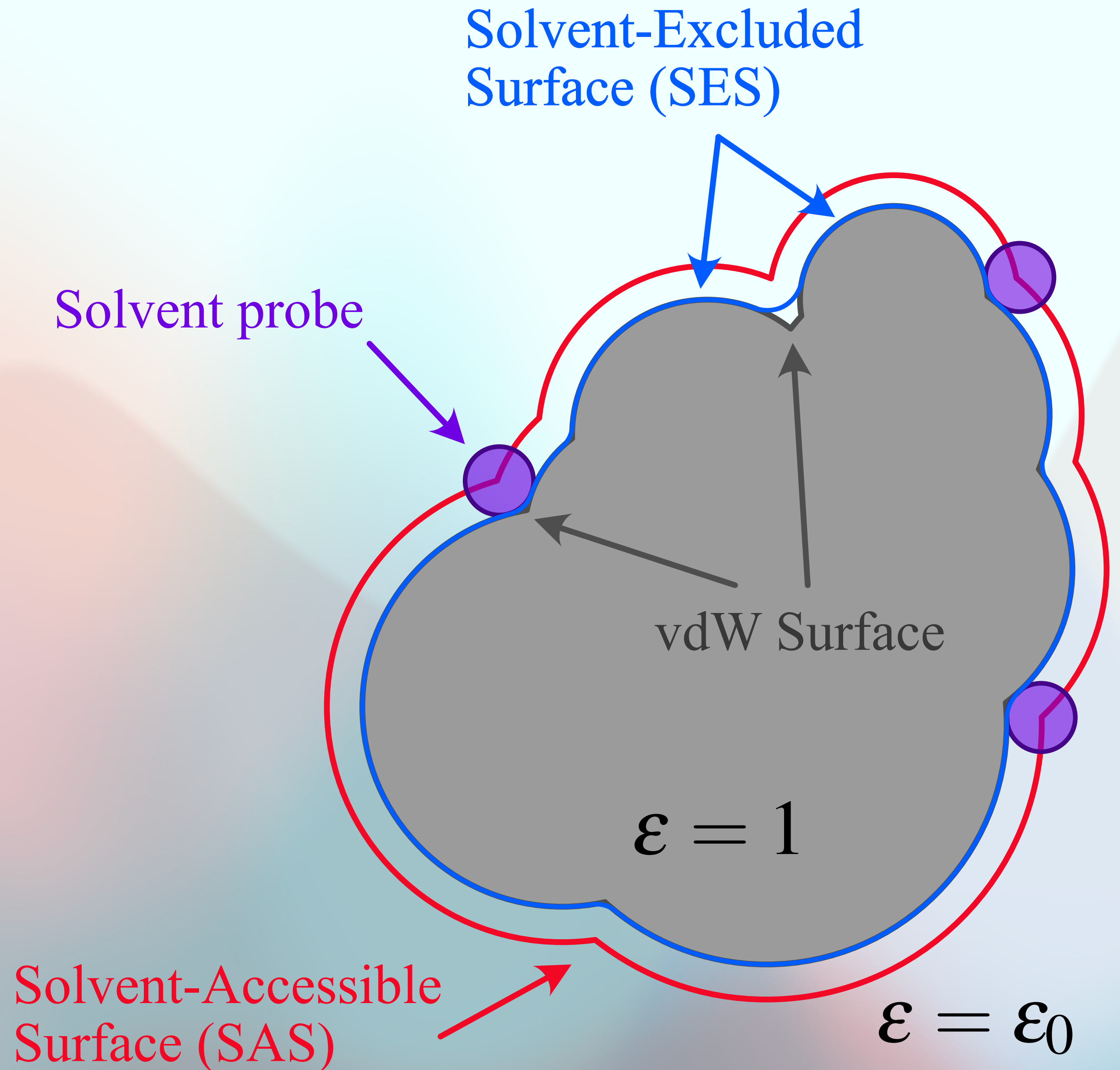
- Puts a solute in a cavity with a dielectric bulk on the outside
- Allows the solute and solvent to polarise each other within the SC(R)F cycles



- Older approaches used spherical cavities and solved equations analytically
- Newer methods involve discretised cavities

Cavity generation

- vdW Surface (vdW)
 - Sum of vdW spheres
- Solvent-excluded Surface (SES)
 - (Connolly)
- Solvent accessible surface (SAS)
 - vdW + solvent probe radius
 - vdW x scaling factor (usually 1.2)
- May include or exclude protons



Choice of Radii

- All are derived from MM parameterisation
- Have the largest effect on the electrostatic term and can act as a scaling factor
- Some options include
 - UFF
 - Gaff
 - Bondi
 - Arlinger
 - etc.
 - (We'll get to SMD later...)

Choice of Radii

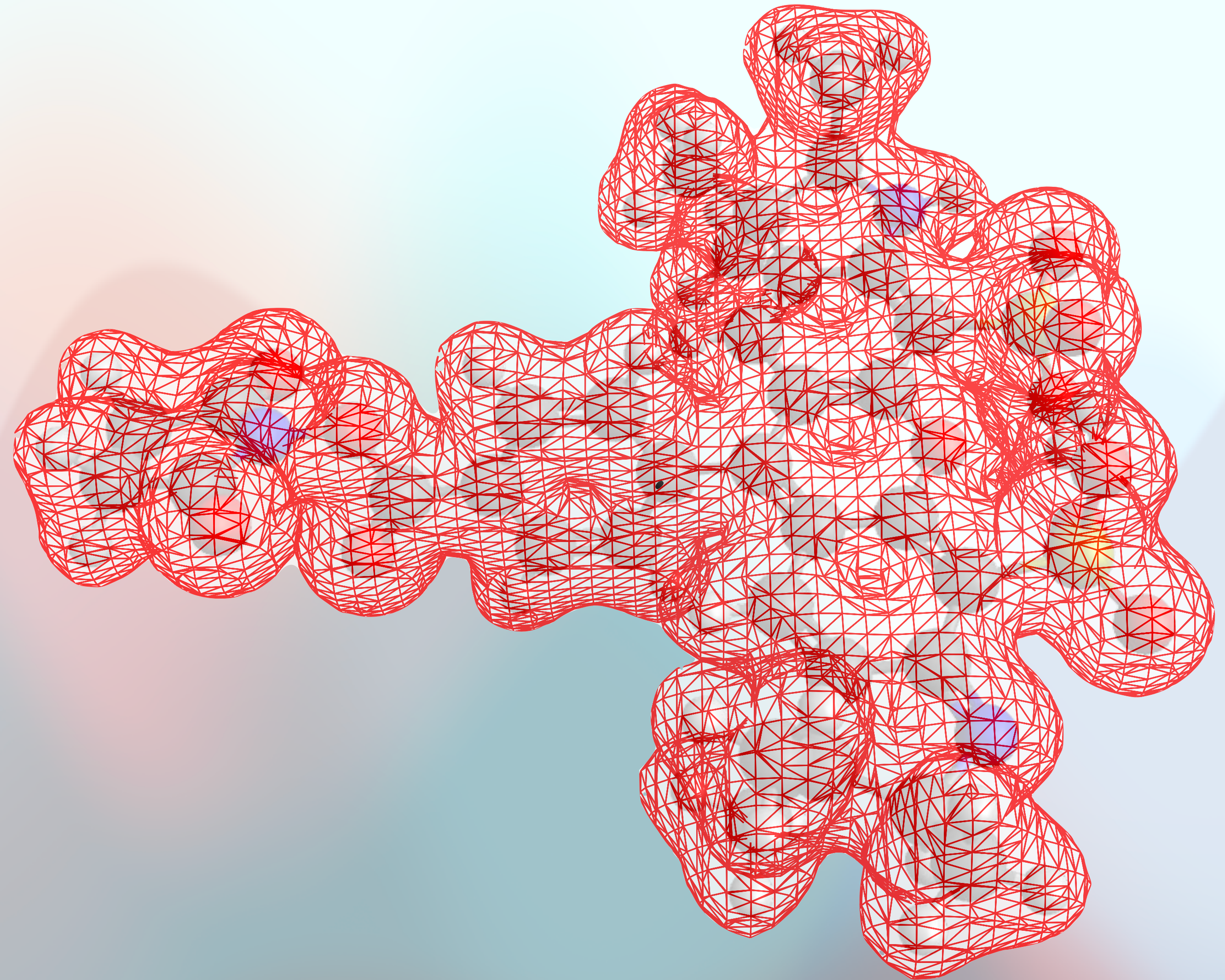
My recommendation

- Use whichever the rest of your model is parameterised for
- These are often used to over-scale electrostatics to cover up for a lack of non-electrostatic terms
- We'll come back to SMD

Cavity discretisation

Isodensity

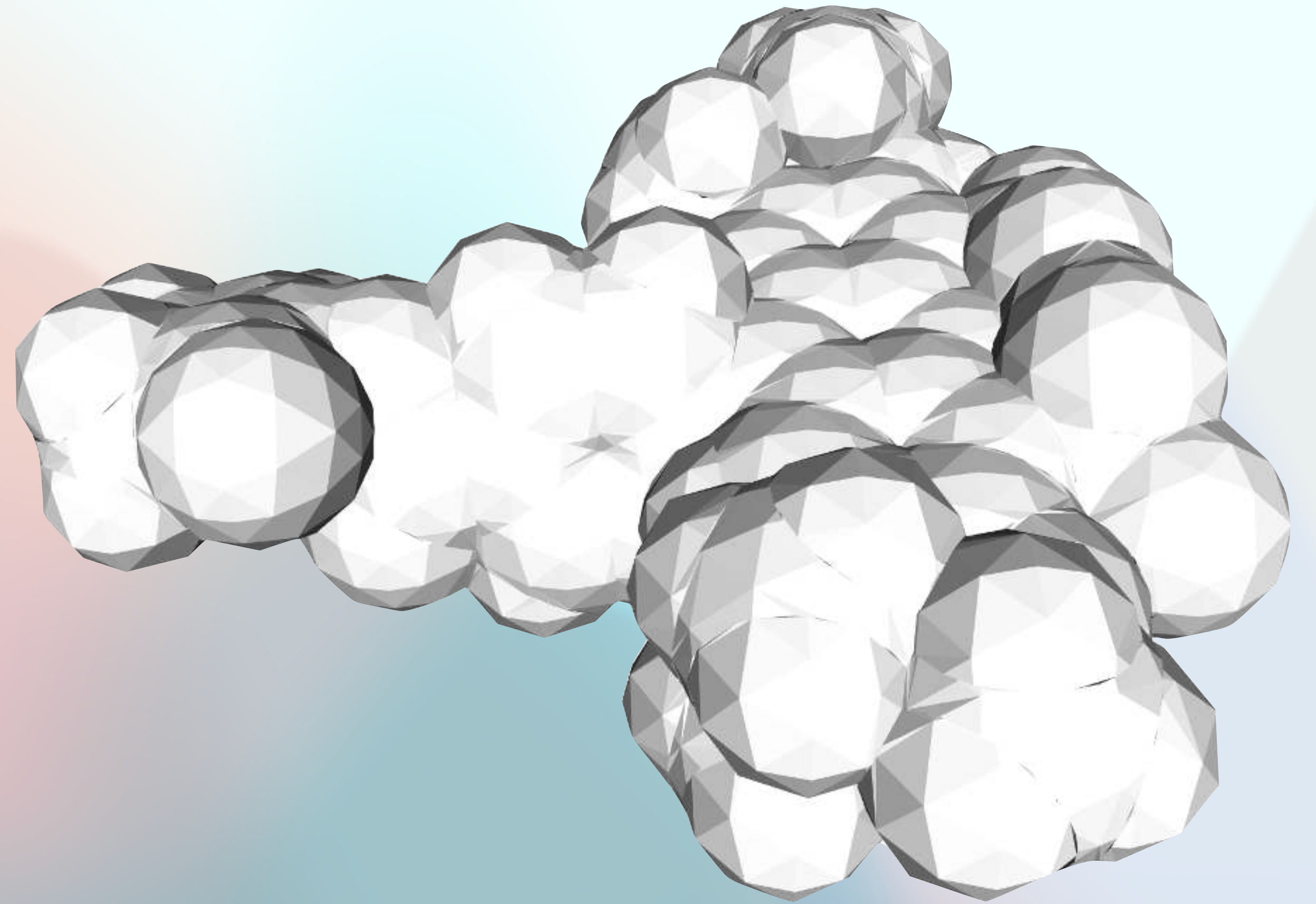
- **Isodensity**
- Tesserae (GEPOL)
- Lebedev (SWIG)



Cavity discretisation

Tesserae

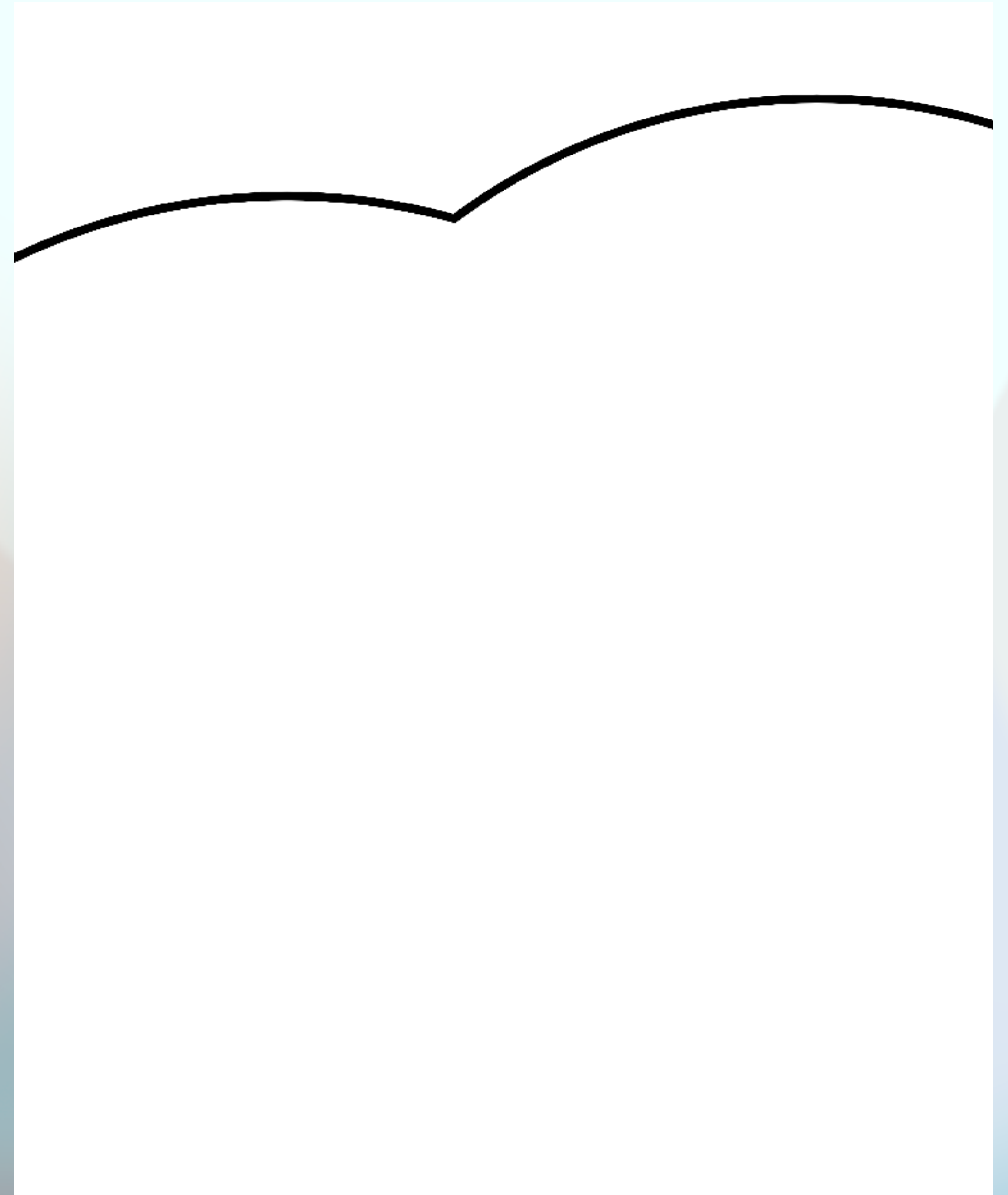
- Isodensity
- **Tesserae (GEPOL)**
- Lebedev (SWIG)



Cavity discretisation

Tesserae - discontinuous

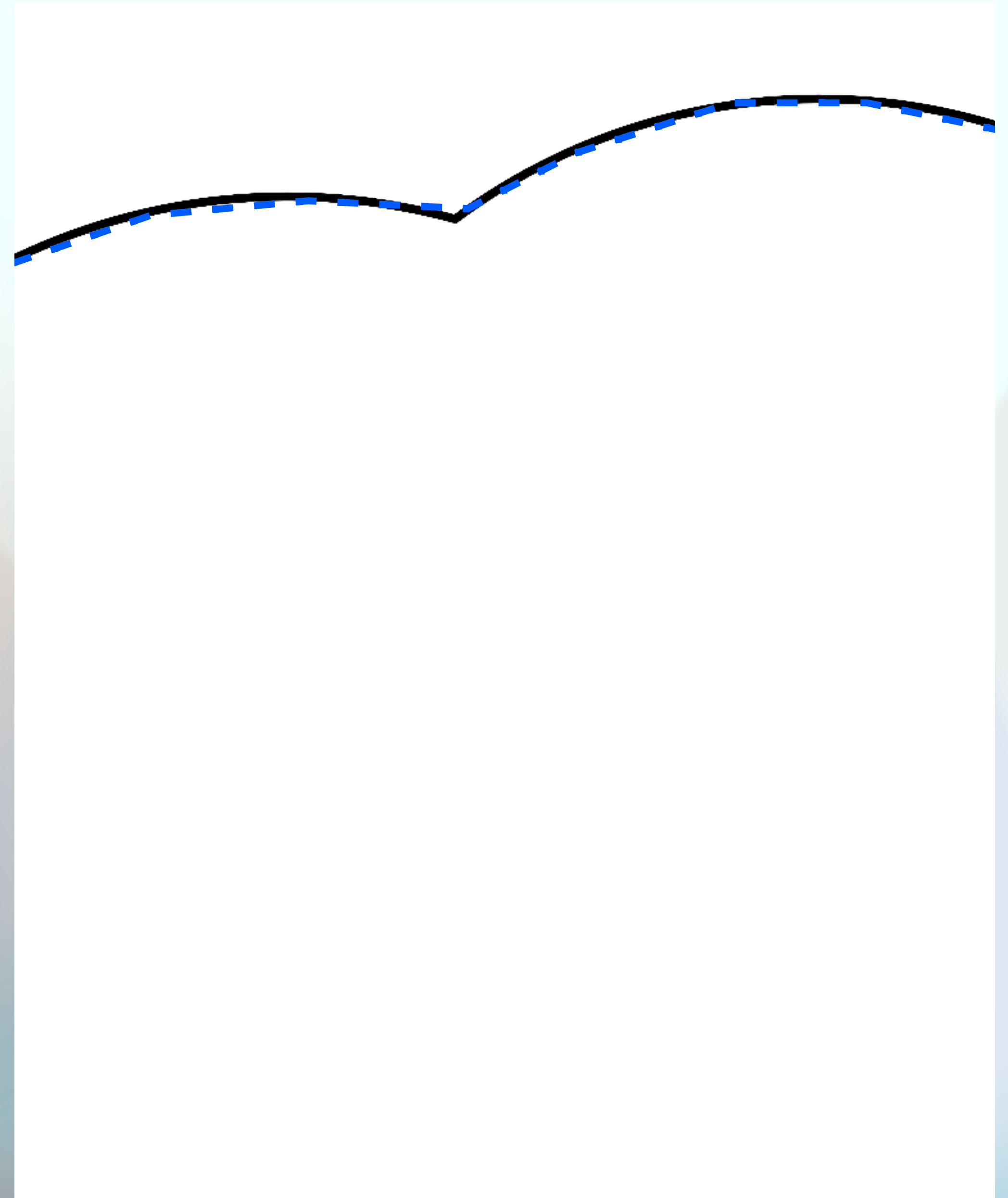
- Start with our surface (SAS, SES, vdW)



Cavity discretisation

Tesserae - discontinuous

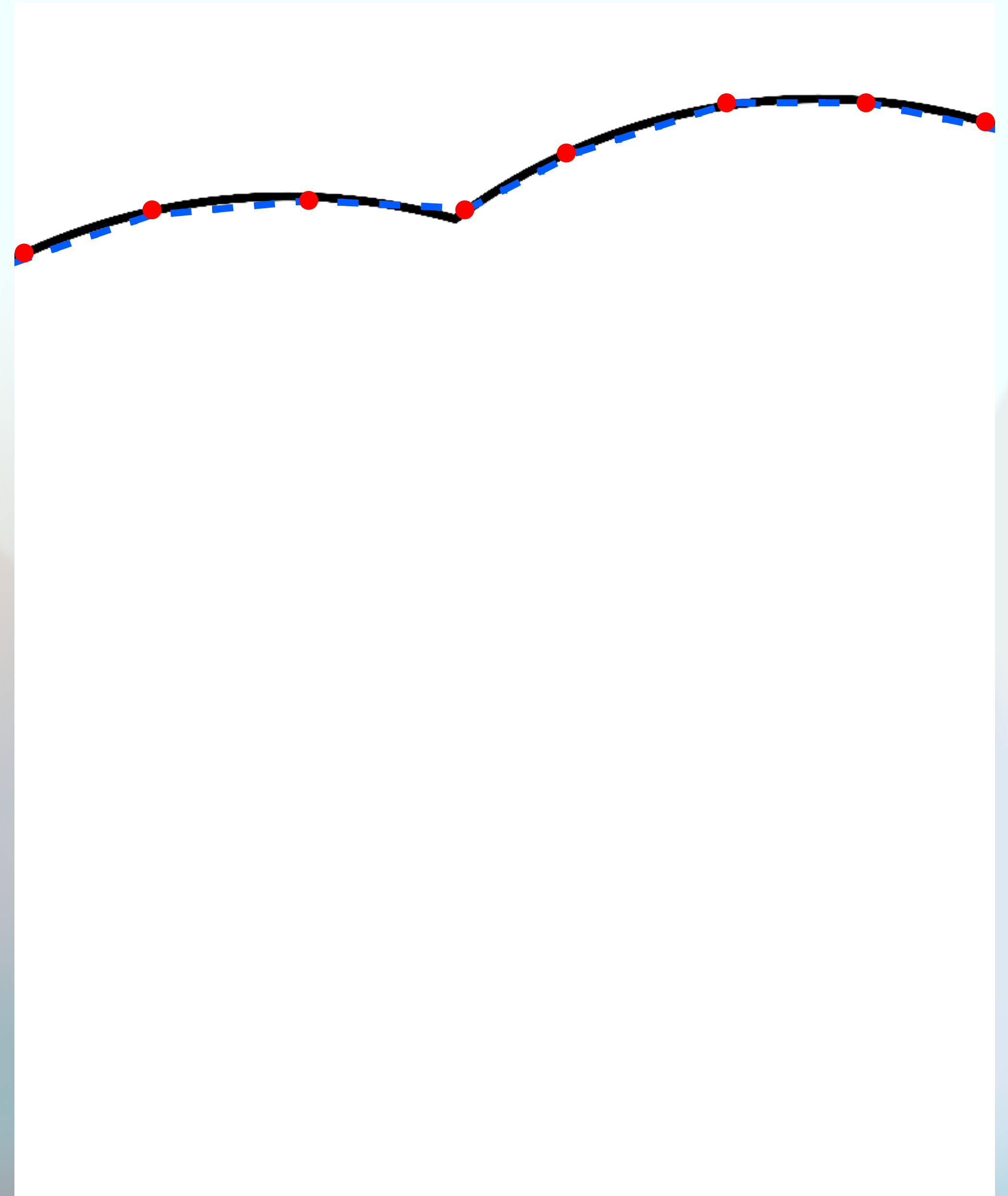
- Start with our surface (SAS, SES, vdW)
- Build our polyhedra surface



Cavity discretisation

Tesserae - discontinuous

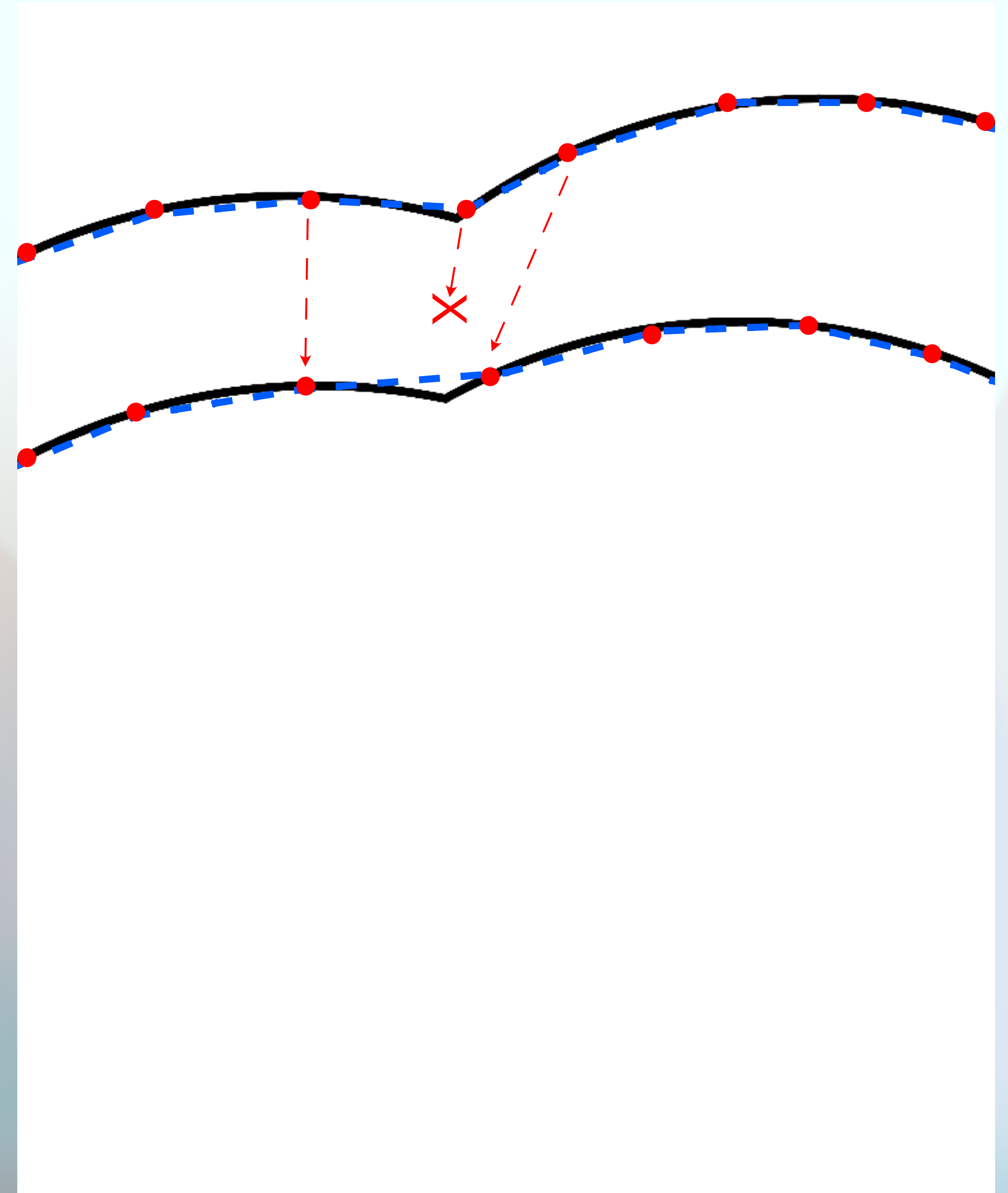
- Start with our surface (SAS, SES, vdW)
- Build our polyhedra surface
- Add our point charges



Cavity discretisation

Tesserae - discontinuous

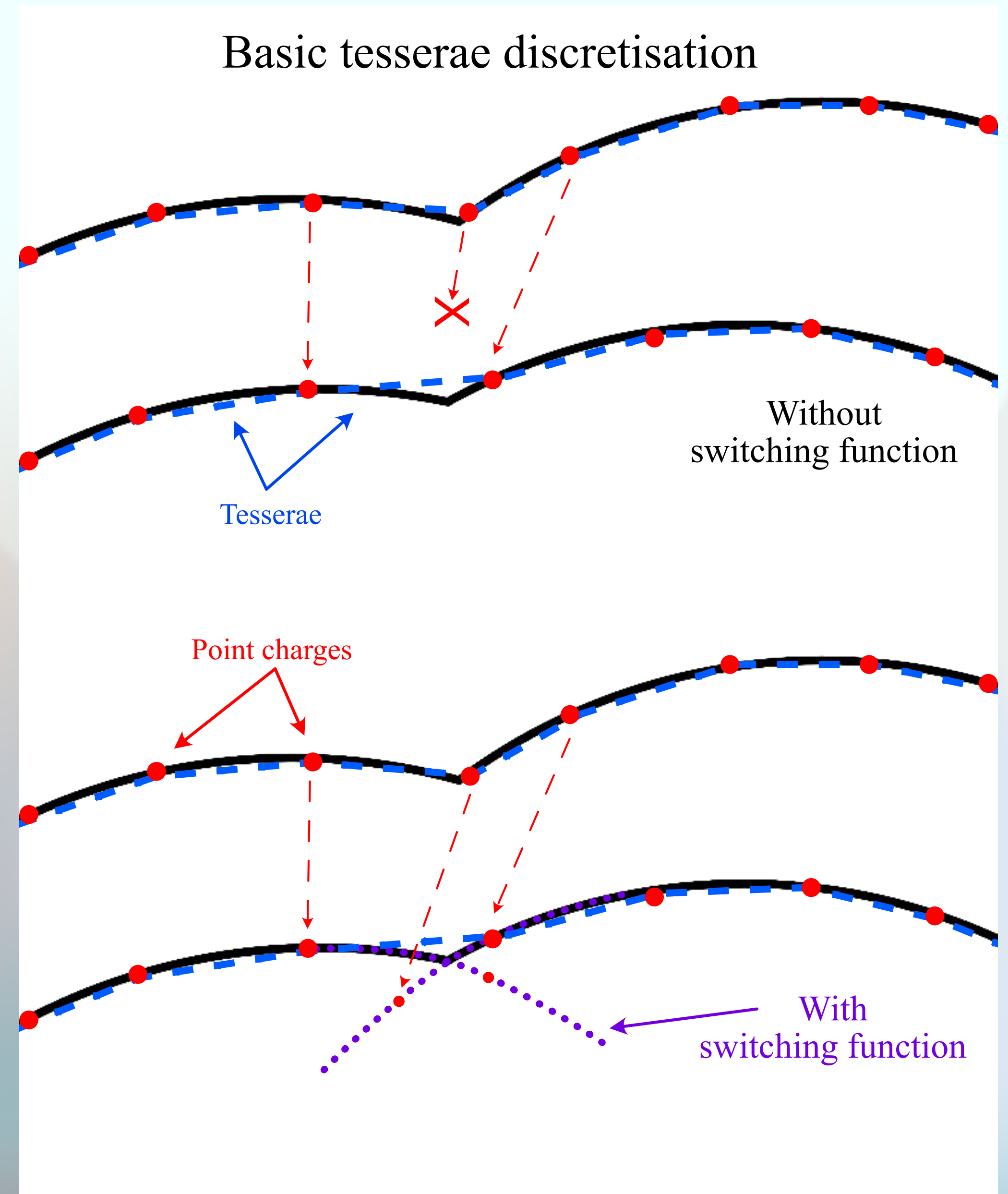
- Start with our surface (SAS, SES, vdW)
- Build our polyhedra surface
- Add our point charges
- Issues:
 - Points disappearing
 - Coulomb spikes as points approach each other



Cavity discretisation

Tesserae - Switching functions!

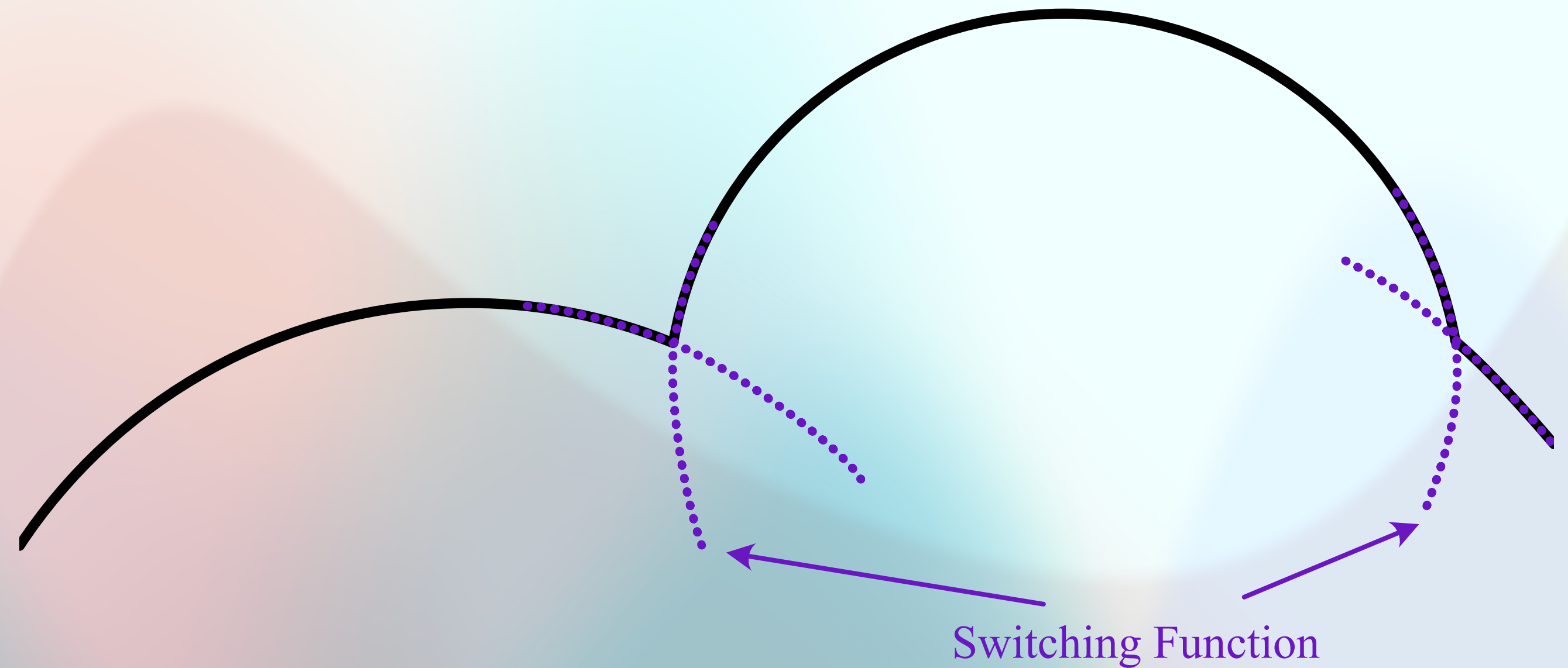
- Switching function
 - Switches “smoothly” between the polyhedra



Cavity discretisation

Lebedev - SWIG

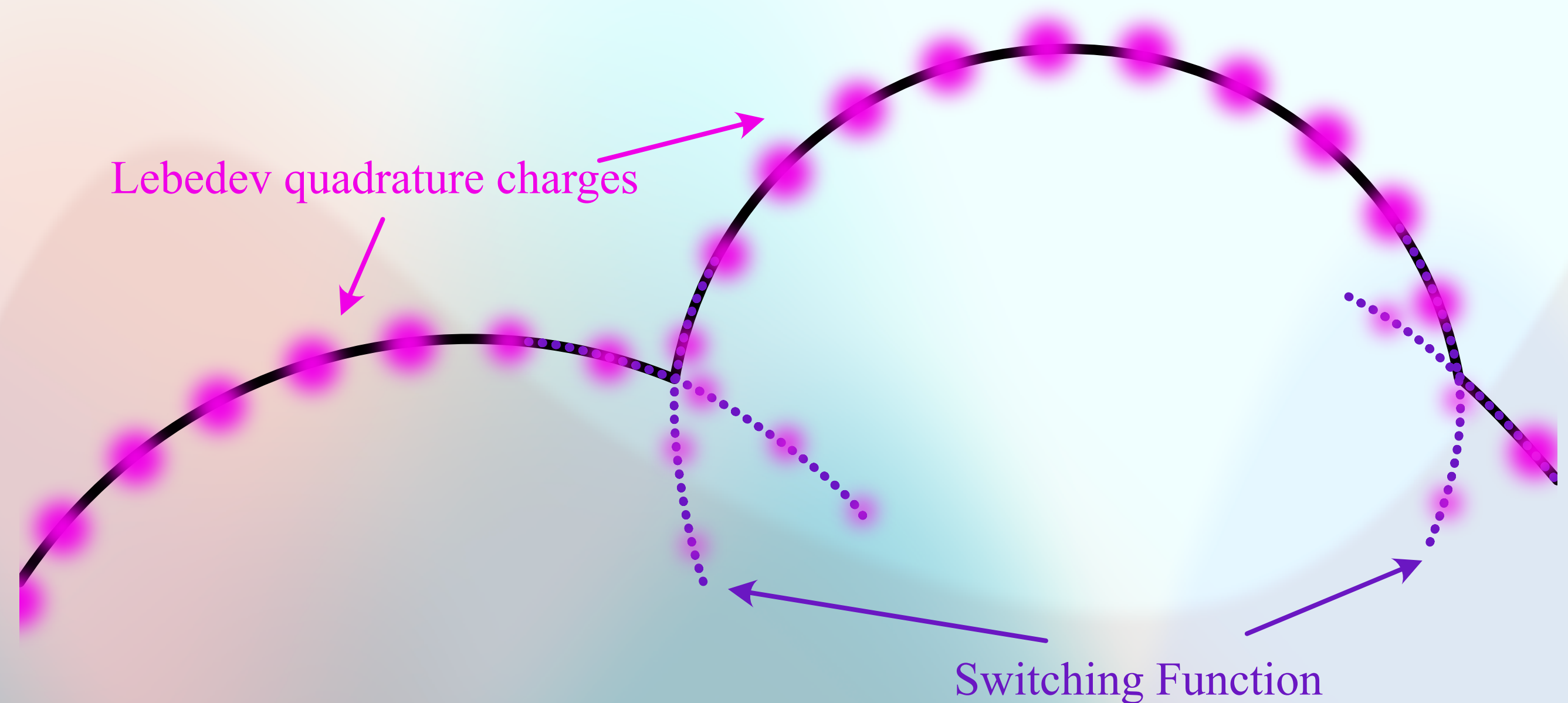
- Starts with our cavity and has a switching function



Cavity discretisation

Lebedev - SWIG

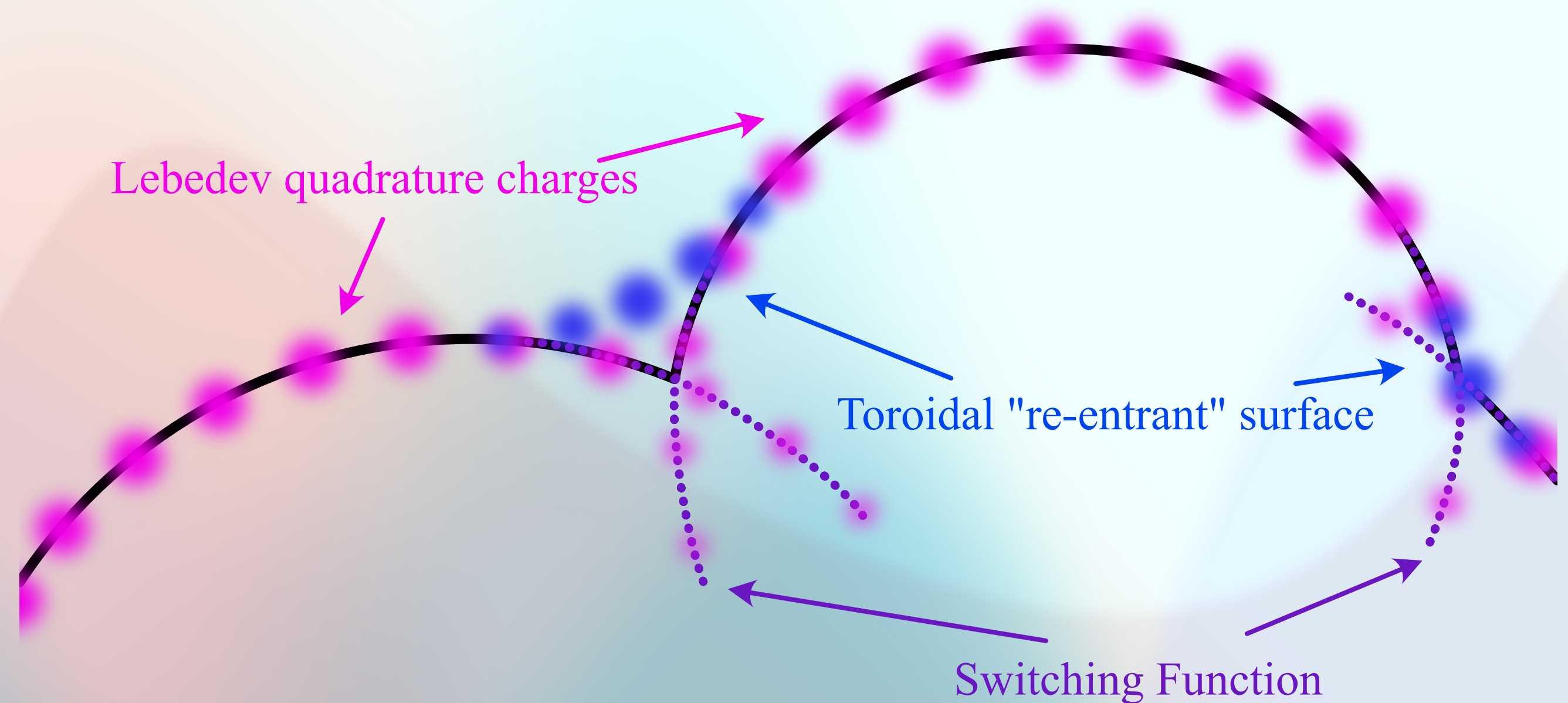
- Starts with our cavity and has a switching function
- Uses Lebedev quadrature to place charges
 - Systematically improvable
- Charges are Gaussian blurred



Cavity discretisation

Lebedev - SWIG

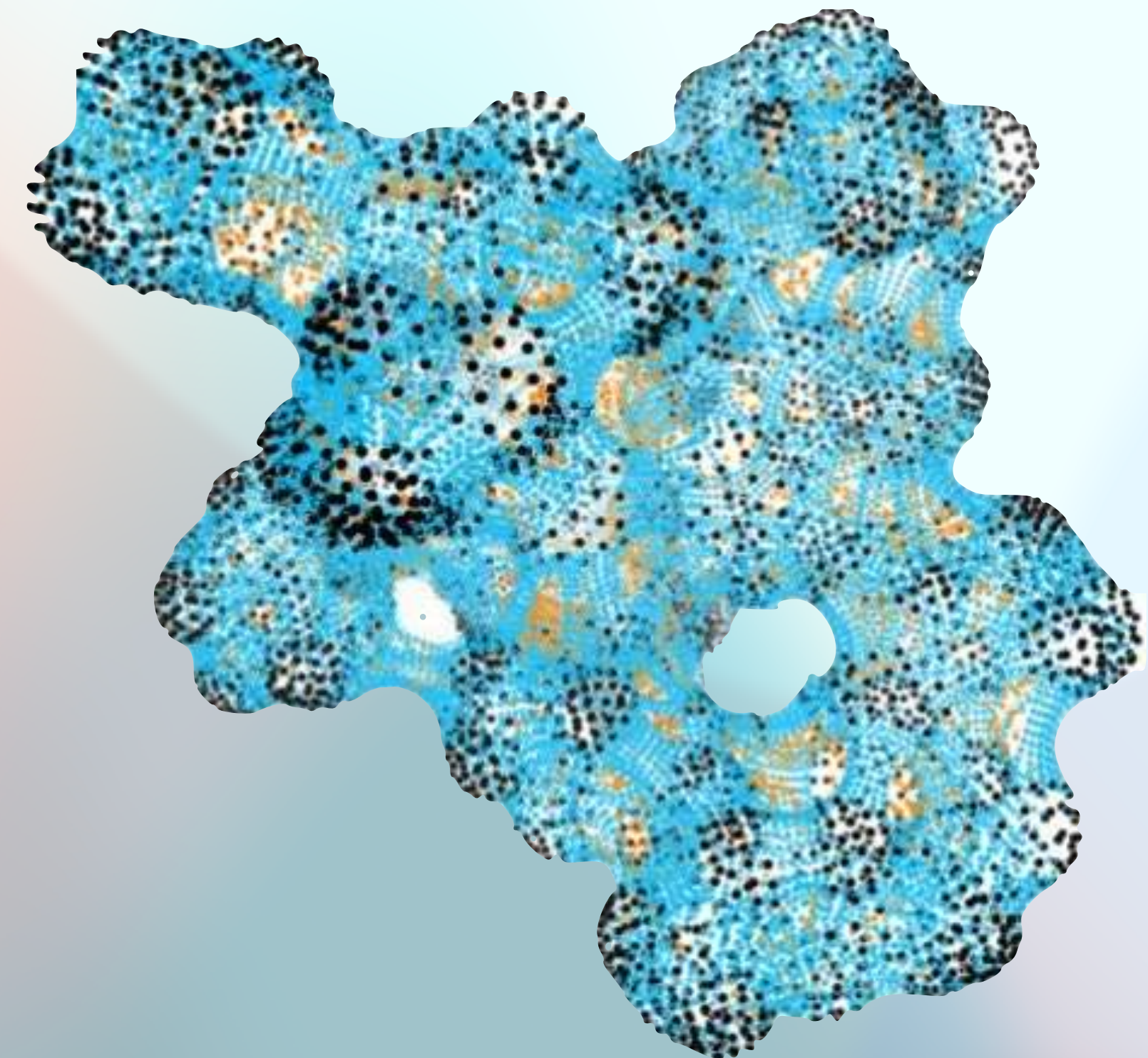
- Starts with our cavity and has a switching function
- Uses Lebedev quadrature to place charges
 - Systematically improvable
- Charges are Gaussian blurred
- Adds in more charges over the intersections



Cavity discretisation

Lebedev - SWIG

- Final points look more like this
 - Black is Lebedev
 - Blue is toroidal
 - Orange is switching



Cavity discretisation

My recommendation

- Isodensity is fantastic for single point calculations, but doesn't have gradients, and thus is not implemented in much.
 - These also overcome outlying charge issues (we'll talk about this soon)
- SWIG is the gold standard atm and is implemented in ORCA and QChem by default
- Switching functions are always a good idea for optimisations, and can reduce SCF convergence issues
- If GEPOL is all you've got, then your software doesn't really care about solvation... maybe consider a different package for this part of your study.

Polarisable Continuum Model formalisms

(For solving the electrostatic term)

- Generalised Born model
- Onsanger
- CPCM
- COSMO
- IEF-PCM
- SS(V)PE

PCM formalisms

Generalised Born

$$\Delta G_Q = -\frac{Q^2}{2\bar{R}} \left(\frac{\epsilon - 1}{\epsilon} \right)$$

- Analytical solution to Poisson eqn
- Requires a spherical cavity with all the charge inside of that cavity
 - Is a big ask for QM calculations
- Model is used by numbered Minnesota models (SMx)
 - The models calculate explicit atomic point charges and put them in a cavity to ensure no charge leakage

PCM formalisms

Onsager

$$\Delta G_Q = - \frac{(\epsilon - 1)\mu^2}{(2\epsilon + 1)\bar{R}^3}$$

- Generalised Born but with dipoles!
 - Not much more useful for QM...
 - Kirkwood took this to multipoles, so that's cool, I guess?

PCM formalisms

CPCM

$$\sigma(s) = -\tilde{f}_\varepsilon(\zeta)\varphi^\rho(s)$$

Where the scaling factor:

$$\tilde{f}_\varepsilon(\zeta) = \frac{\varepsilon_s - 1}{\varepsilon_s + \zeta}$$

- Conductor-like PCM
- Solves the SC(R)F equations for $\varepsilon = \infty$ (a conductor)
- Scales the result for $\varepsilon = \varepsilon_0$
 - $\sigma(s)$ are the resulting charges from our solute
 - $\varphi^\rho(s)$ is the electrostatic potential of the solute from the Schrödinger eqn
 - $\zeta = 0$ for CPCM

Please don't make me go through the precursory equations...

PCM formalisms

COSMO

$$\sigma(s) = -\tilde{f}_\varepsilon(\zeta)\varphi^\rho(s)$$

Where the scaling factor:

$$\tilde{f}_\varepsilon(\zeta) = \frac{\varepsilon_s - 1}{\varepsilon_s + \zeta}$$

- Very similar to CPCM in how it works, but uses $\zeta = 0.5$ for COSMO
- The *true* form of COSMO as described by Klamt and Jonas has a double cavity
 - SES (smoothed vdW) for the main screening charges
 - SES + Solvent probe radii X0.95 for the outer cavity
 - Uses this to capture any outlying charge
- Most software just uses CPCM with $\zeta = 0.5$, with an SAS cavity and call it COSMO

PCM formalisms

IEF-PCM

$$\left[\left(\frac{2\pi}{f_\varepsilon} \right) \hat{1} - \hat{D} \right] \hat{S} \sigma(s) = (-2\pi \hat{1} + \hat{D}) \varphi^\rho(s)$$

- Integral equation formalism PCM
- Is an “exact” reformulation of the classical continuum electrostatics problem
 - ...assuming that all the solute charge is contained within the cavity
 - For QM solutes, there is always escaped charge for realistic cavities

**This is where I REALLY can't
explain the maths all that well...**

PCM formalisms

SS(V)PE

- Surface and simulation of volume polarisation for electrostatics
- Corrects IEF-PCM by reformulating the equations to assume that there's going to be a certain amount of outlying charge.
- Assumes that the dielectric boundary ESP is going to be accompanied by a “volume polarisation” arising from outlying charge
- A second surface charge must therefore exist that balances out the volume polarisation that is taken into account in this model

Polarisable Continuum Model formalisms

My recommendation

- Generalised Born model and Onsanger (and Kirkwood) are obsolete - Don't use them
- CPCM and COSMO are pretty much equivalent and are both good for $\epsilon_0 > 10$
 - These will be equivalent to IEF-PCF as $\epsilon_0 \rightarrow \infty$
- IEF-PCM is generally better than SS(V)PE where standard vdW cavities are used
 - They behave almost identically for isodensity cavities
 - Also almost identical when omitting protons from the cavity generation
 - Use IEF-PCM or SSV(P)E for $\epsilon_0 < 10$

Non-Electrostatic Terms

- Solves for “Other” terms
 - Cavitation - The energy required to form the cavity (based on γ)
 - Dispersion - (based on α)
 - Pauli repulsion
 - Hydrogen-Bonding - between the solute and solvent
- All models are parameterised to some extent, either by making specific models from bespoke datasets, or based on MM force fields

Non-Electrostatic Terms

Complexities

- “Everything is electrostatics...”
- The different terms are all very intertwined
 - Hydrogen bonding is a part of electrostatics
 - Dispersion and repulsion are very intertwined and highly dependent on the cavity
 - The cavity largely stems from non-electrostatic repulsion, yet the cavity is fundamental to the electrostatic term
 - All of the properties, including the PCM cavity are solvent dependent
- **Requires us to treat all terms in unison - All the terms must be parameterised together**

Non-Electrostatic Terms

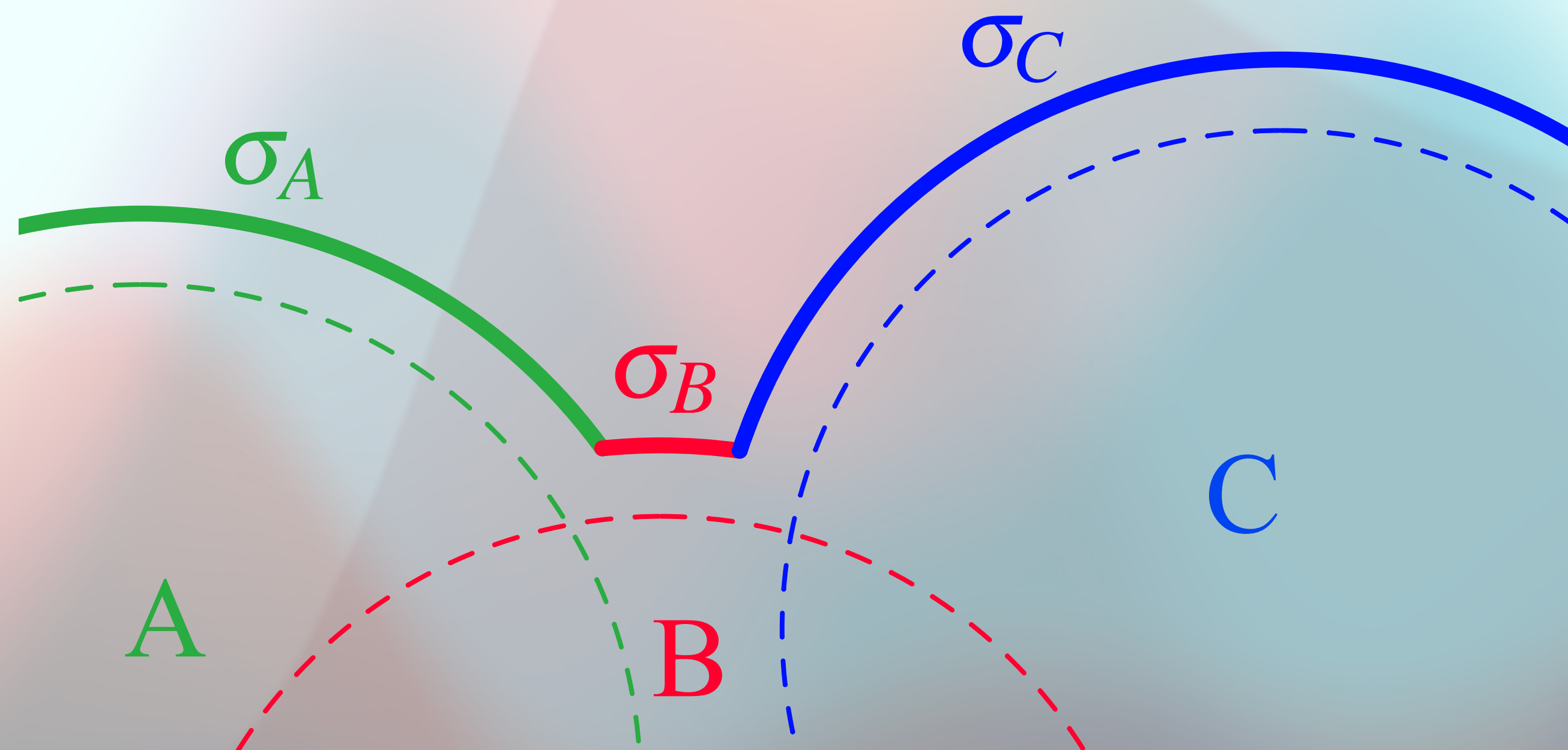
MM based dispersion/repulsion

- Typically use Lennard-Jones or Buckingham parameters to calculate the dispersion repulsion term
- These are VERY force field dependent, and require the solute to be explicitly parameterised (LJ params for MM are often pretty dodgy)
- Not a good approach, and fickle to use

Non-Electrostatic Terms

SASA based methods

- Solvent accessible surface area (SASA)
- Integrate over the exposed surface of each atom and use atom-specific parameters (σ) to define the non-electrostatic terms



Non-Electrostatic Terms

SASA based methods - SMx

- The most known/successful SASA approach are the SMx approaches from Minnesota (Truhlar, Cramer, and co.)
- The numerical SMs methods (SM8, SM12, etc.) use the GB cavity and their parameterised charge models they call CMx (so creative, I know...)
- All use the SASA approach to calculate a Cavitation/Dispersion/Solvent-structure (CDS) term
- VERY transferable to new solvents, very accurate for species within the Minnesota training dataset (most organics)
- Elegantly simple maths!

Non-Electrostatic Terms

SASA based methods - SMx

- Uses physical solvent descriptors

- ϵ = dielectric constant at 298.15K
- n^2 = square of the refractive index (ϵ_∞)
- α = Abraham's H-bonding acidity
- β = Abraham's H-bonding basicity
- γ = Macroscopic surface tension of the solvent
- ϕ = Fraction of solvent atoms that are aromatic
- ψ = Fraction of solvent atoms that are electronegative halogens (F, Cl, or Br)

$$\sigma^{[M]} = \tilde{\sigma}^{[\gamma]}(\gamma/\gamma_0) + \tilde{\sigma}^{[\phi^2]}\phi^2 + \tilde{\sigma}^{[\psi^2]}\psi^2 + \tilde{\sigma}^{[\beta^2]}\beta^2$$

$$\tilde{\sigma}_i = \tilde{\sigma}_i^{[n]}n + \tilde{\sigma}_i^{[\alpha]}\alpha + \tilde{\sigma}_i^{[\beta]}\beta$$

- All the physical terms are linear combinations of descriptors and respective weights
- IEF-PCM is used with vdW radii that are parameterised and scaled according to α
- Different radii are used for the SASA
- Non-electrostatic terms are weighted sums of these linear combinations according to the SASA

Non-Electrostatic Terms

“Physical methods” — Different approaches

- Attempt to be more physically rigorous than SMx methods
- Calculate dispersion/repulsion from the frequency dependent polarisability of the solute and converts it into a C_6 coefficient (all QM methods)
- Cavitation from scaled particle theory solvation energies
- Using VV10 dispersion with a bulk solvent density
 - Requires integration of the volume, not just the surface area
- Repulsion from interpenetration of non-bonded densities

Firing off some physicsy buzzwords here

Non-Electrostatic Terms

“Physical methods” – CMIRS

- Contains five empirical parameters for a solvent...
 - Which have only been calculated for benzene, cyclohexane, water, DMSO and ACN
- Uses isodensity SS(V)PE for PCM
- Is more accurate than SMD
- Black box in implementation

Non-Electrostatic Terms

Black Box - COSMO-RS

- COSMO-“Real Solvent”
- Another black box model
- Proprietary, and only works within cosmotherm, with input files generated from other QM packages (e.g. Gaussian)
- Completely closed black box

Non-Electrostatic Terms

My recommendation

- SMD is pretty much the best for speed and is implemented in ORCA, Gaussian, GAMESS, QChem, etc.
- MM based models - do not touch
- CMIRS - Better than SMD, but no gradients due to using isodensity cavity and limited solvent availability
 - Only implemented in GAMESS and QChem
- COSMO-RS - only good for industrial applications due to VERY black box nature
- Not mentioned - (1D/3D)RISM - Only implemented in ADF, not discussed much in literature

What about Correlated methods

The “Perturbation to...” model

- Solvation in correlation becomes more tricky because you have to consider when to apply your solvation in relation to your post-SCF treatment, and to what level you’re going to make it self consistent.



Ground state summary

- The only big thing here to take away is that there isn't a huge amount of consistency between packages and implementations, and not all implementations are made equal
- It's extremely easy to get "good" results through overcounting one term to account for not including another
- Any method that doesn't have non-electrostatic terms is incomplete
 - These terms cannot be mixed and matched
- Gaussian isn't specific about which terms it includes and seems to include non-electrostatic terms in CPCM calculations without specifying

When in doubt

For the ground state

- SMD + IEF-PC + SWIG (available in Q-Chem)
- SMD + CPCM + SWIG (available in ORCA) - maybe not for $\epsilon < 10$
- SMD + IEF-PCM (available in GAMESS and Gaussian)
- SMD + CPCM (available in NWChem) - maybe not for $\epsilon < 10$
- Not recommended but functional:
 - PySCF - GEPOLE + dd-COSMO (scales better than COSMO) - no non-electrostatic terms
- Not good for solvation :
 - Psi4 - GEPOLE + CPCM/IEF-PCM - numerical gradients only, no non-electrostatics

My opinions are biased

- I don't care about getting exact ΔG_{solv}° (sorry Chris Cramer)
- I don't see a method without analytical gradients as being practical
- Methods that require external software, or black box approaches are cumbersome and unscientific imo.

Solvation Models for Excited States



Excited states

(In general)

- Two main methods for calculating excited states using QM
 - Linear response theory (LR)- Used for perturbing the ground state wfn
 - Equations of motion (EoM) - Mostly implemented in correlated methods
- I might come back to EoM Methods when I talk about PTED/PTES...

Excited states

TD-DFT (slide “borrowed” form Lars Goerigk)

Matrix: Single particle excitations

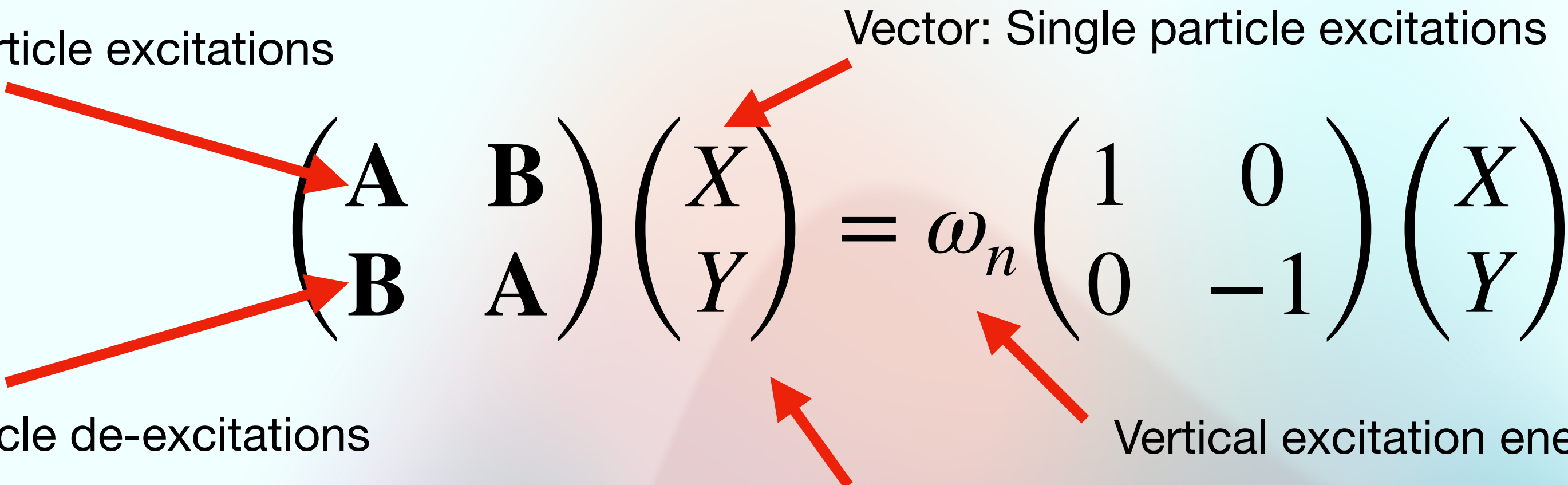
Vector: Single particle excitations

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B} & \mathbf{A} \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix} = \omega_n \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \begin{pmatrix} X \\ Y \end{pmatrix}$$

Matrix: Single particle de-excitations

Vertical excitation energy of state n

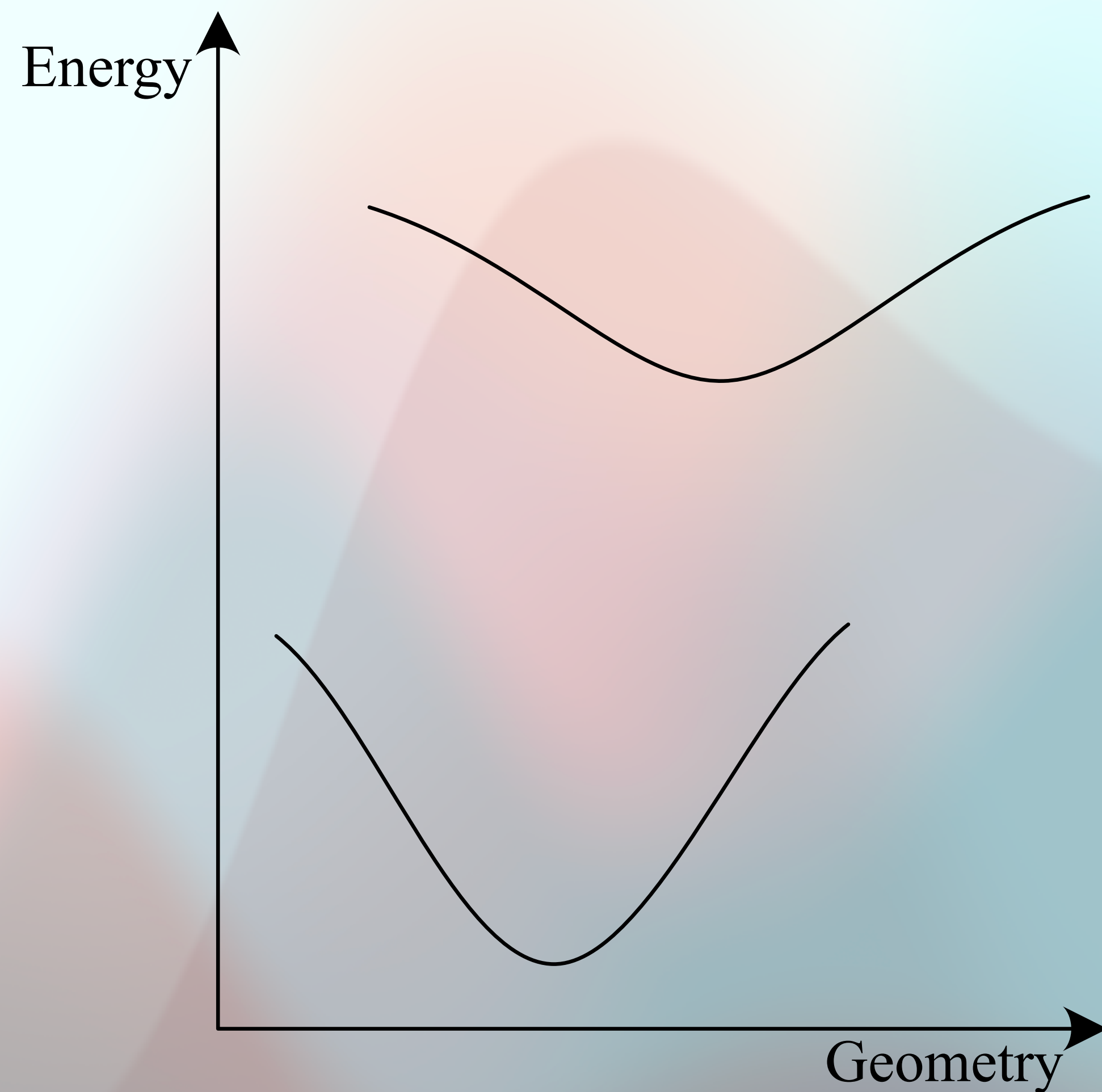
Vector: Single particle de-excitations



- Is an eigenvalue problem that we can solve self consistently and diagonalise for limited roots using the Davidson method
- \mathbf{A} and \mathbf{B} rely on converged ground-state orbitals and xc kernel
- If we ignore \mathbf{B} , ($\mathbf{B} = \mathbf{0}$) we get the Tamm-Dancoff Approximation

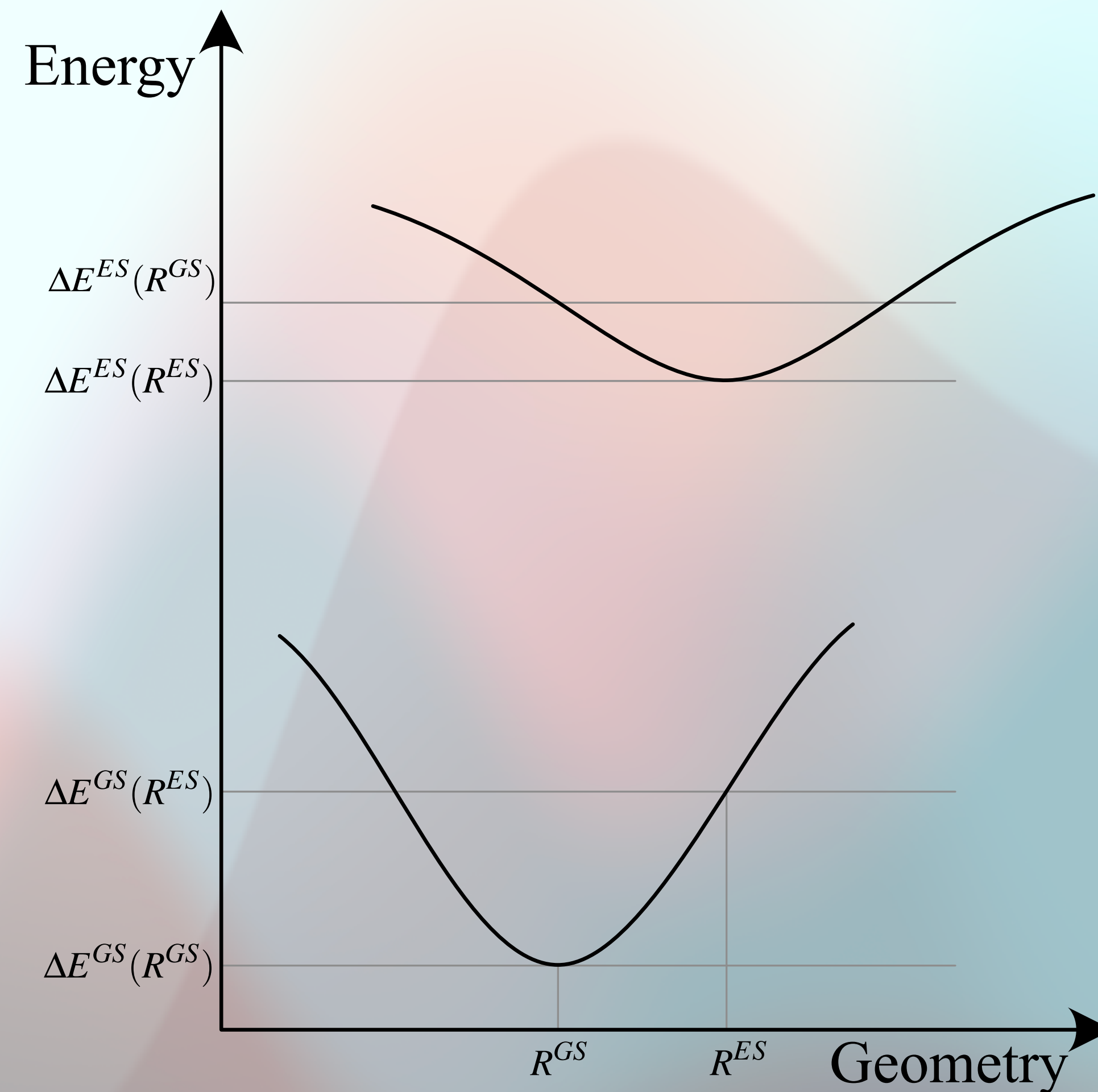
Excited states

Vertical transition model



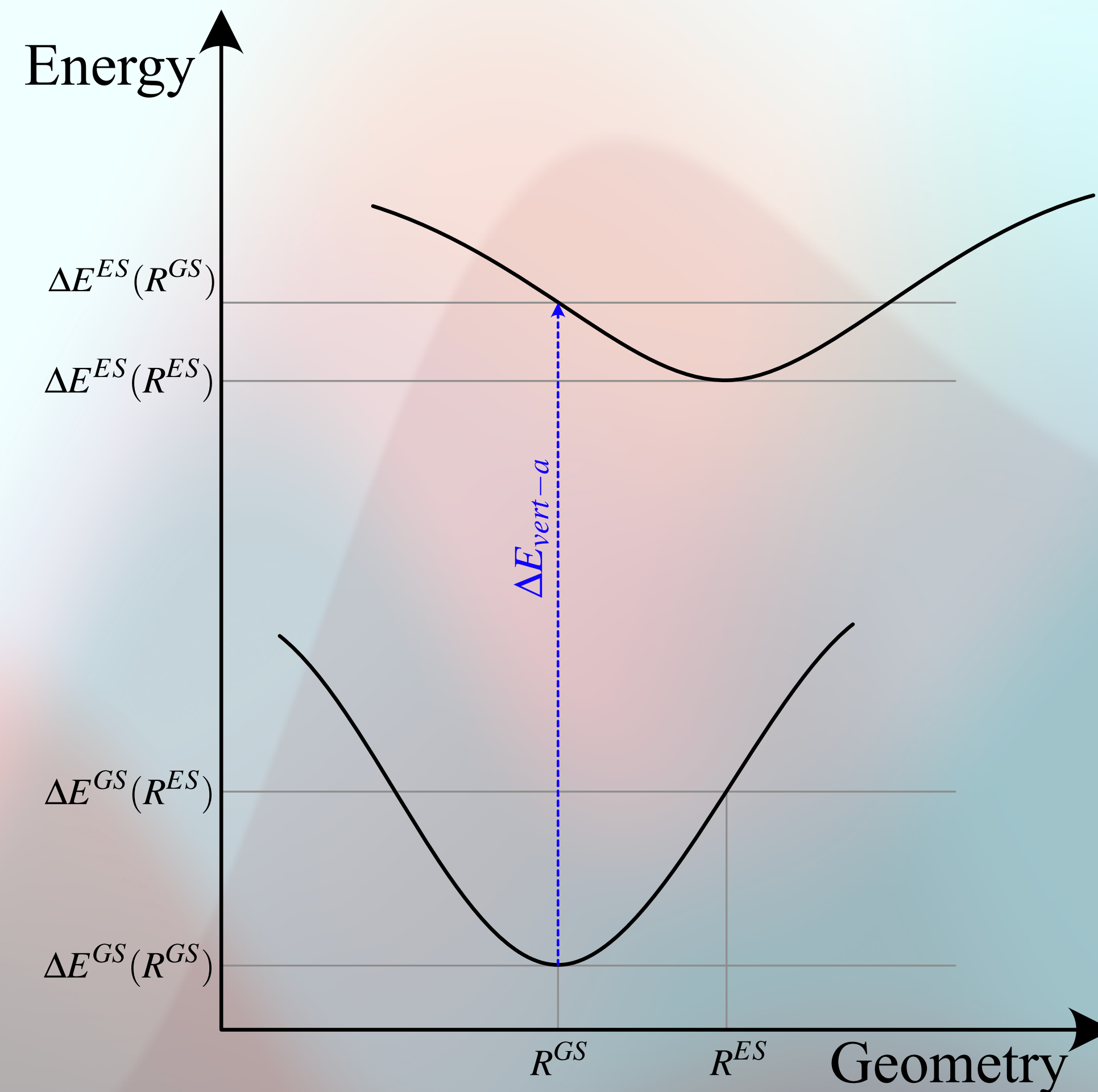
Excited states

Vertical transition model



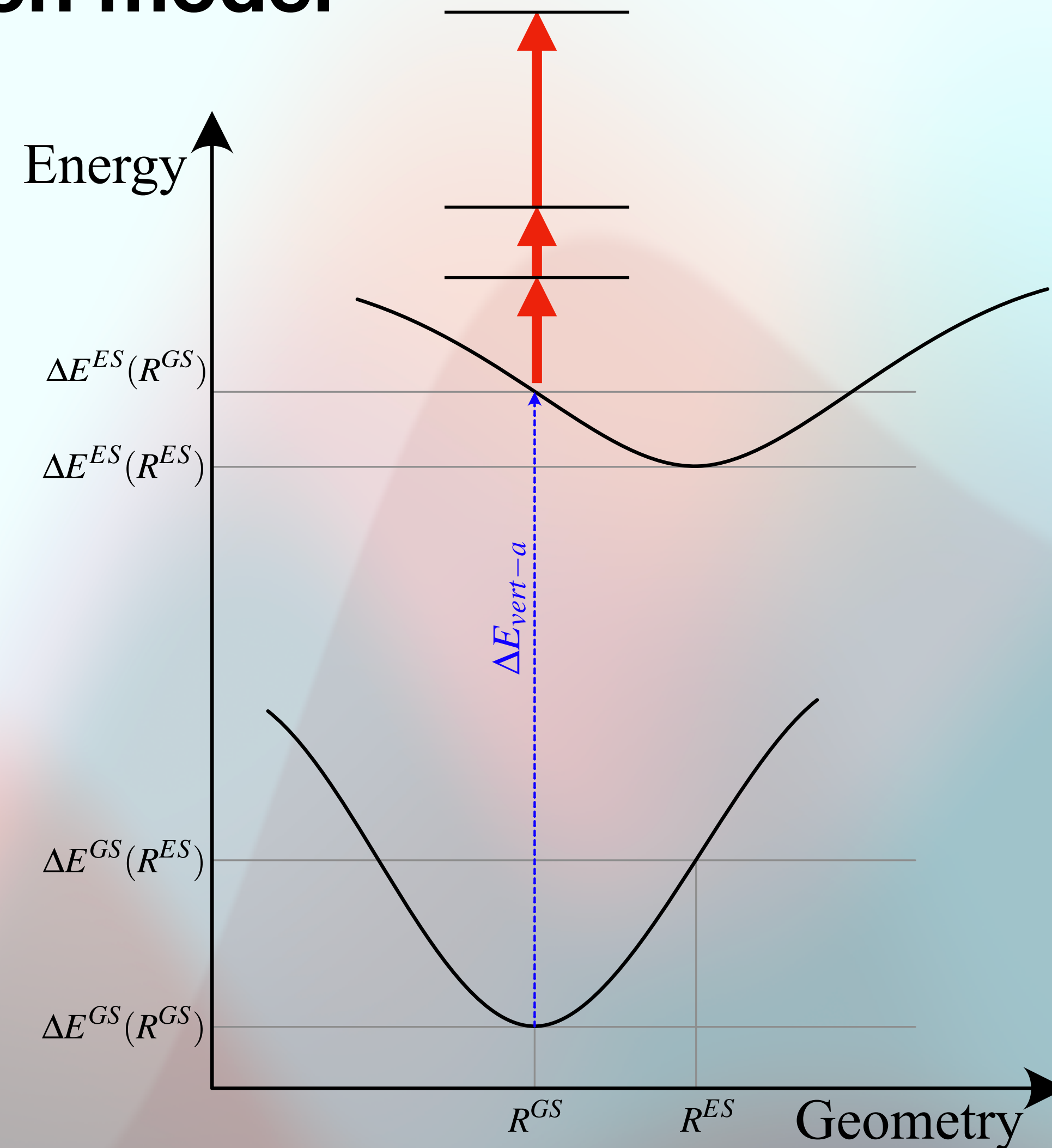
Excited states

Vertical transition model



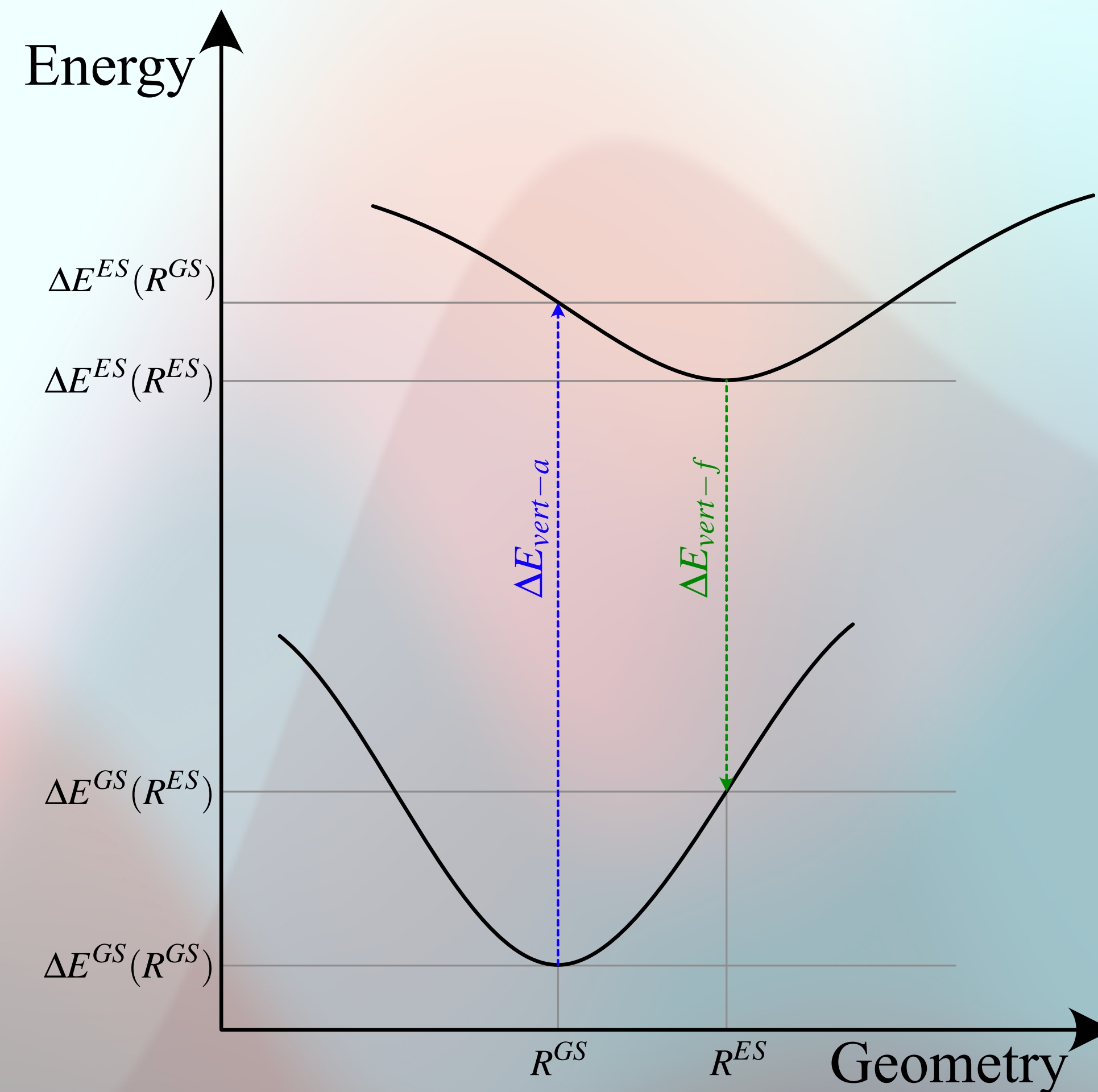
Excited states

Vertical transition model



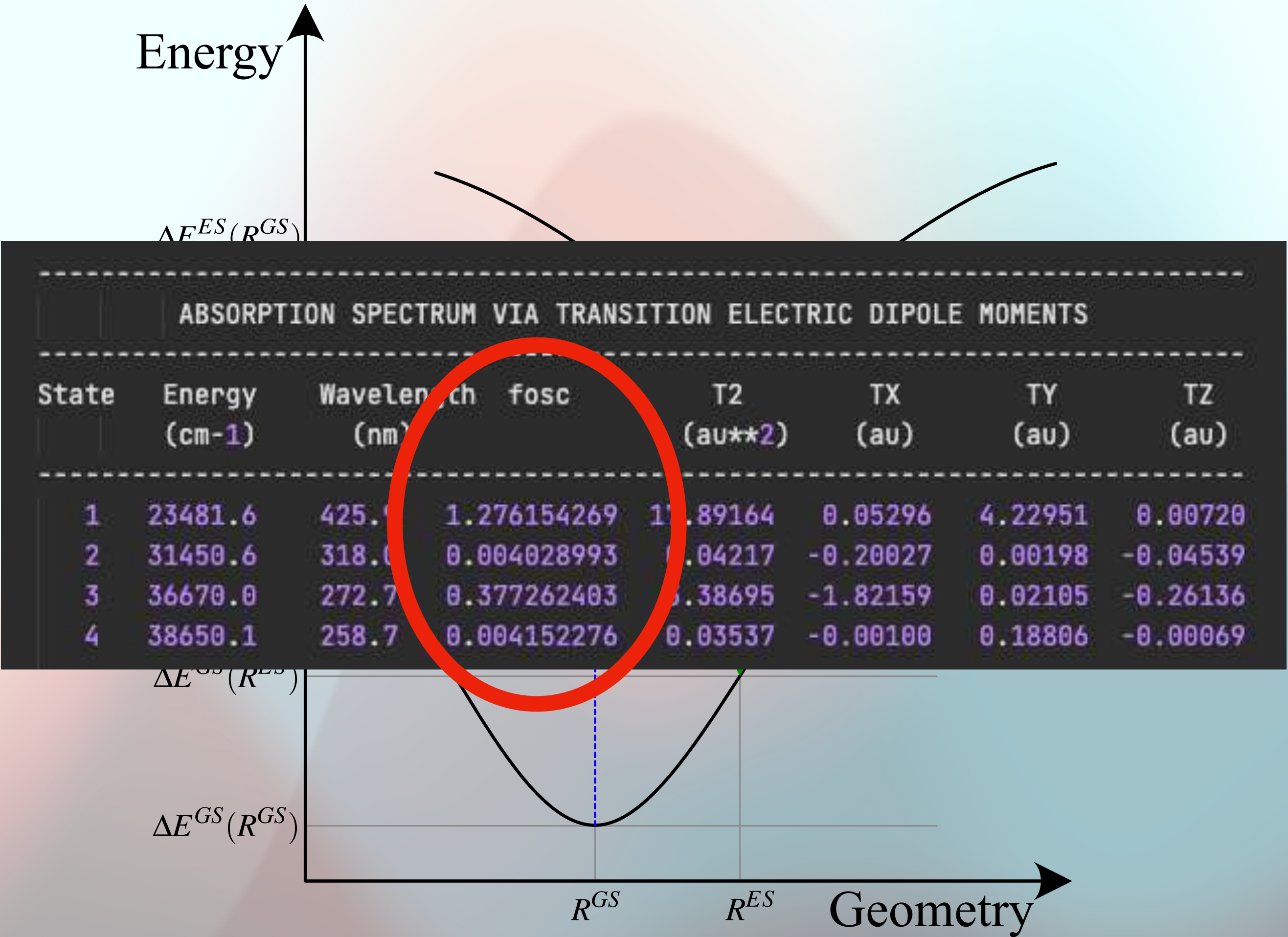
Excited states

Vertical transition model



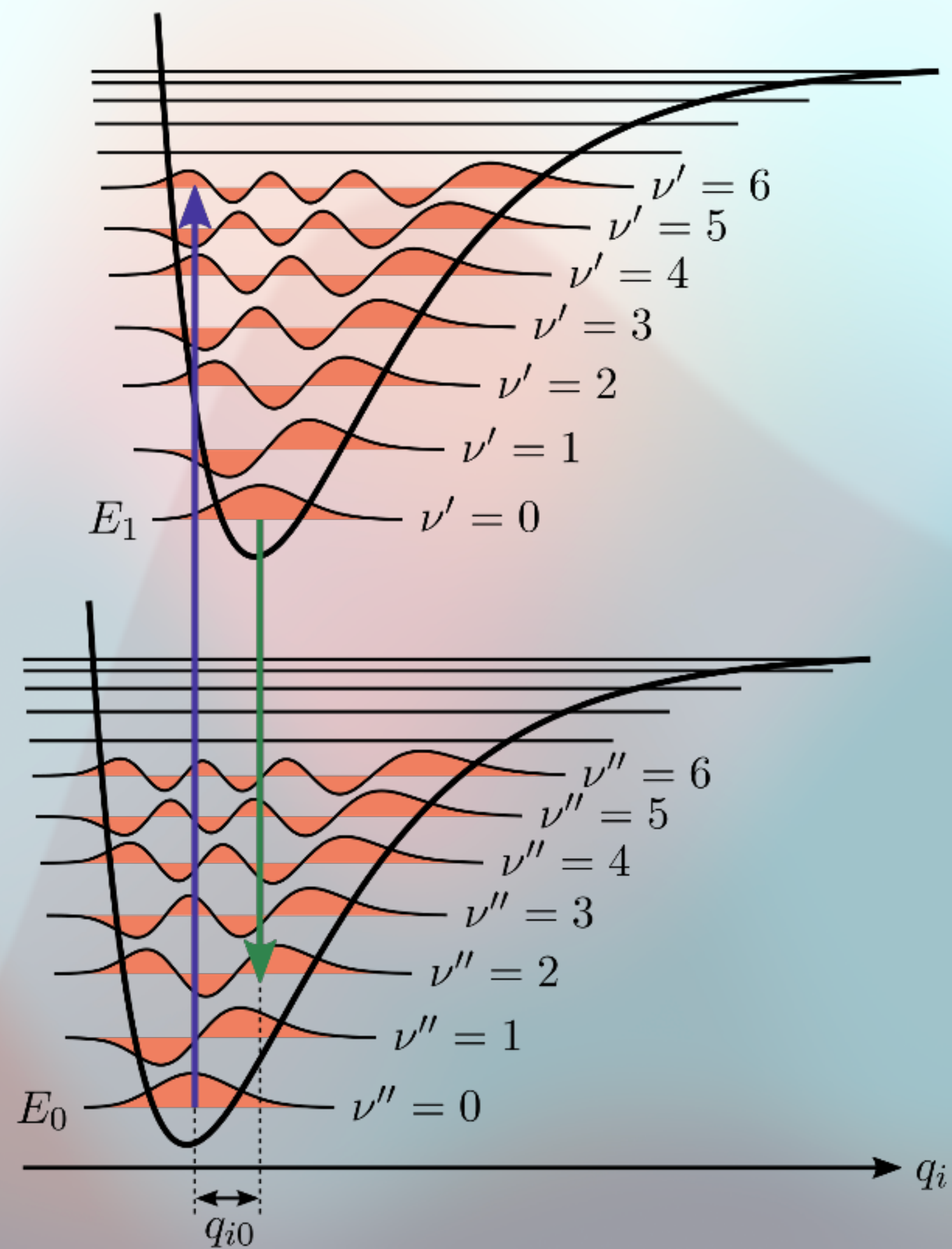
Excited states

Vertical transition model



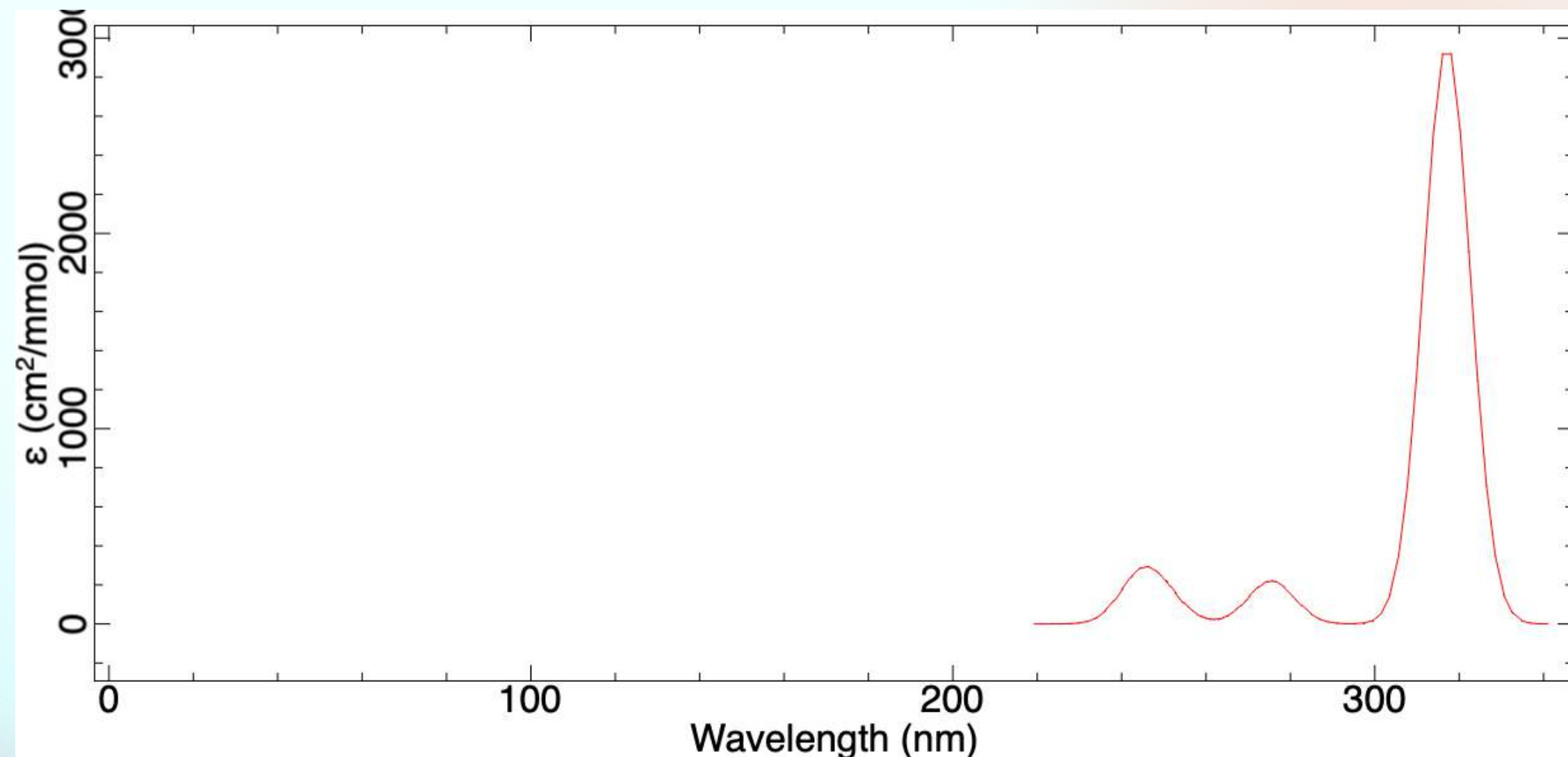
Excited states

Vertical transition model

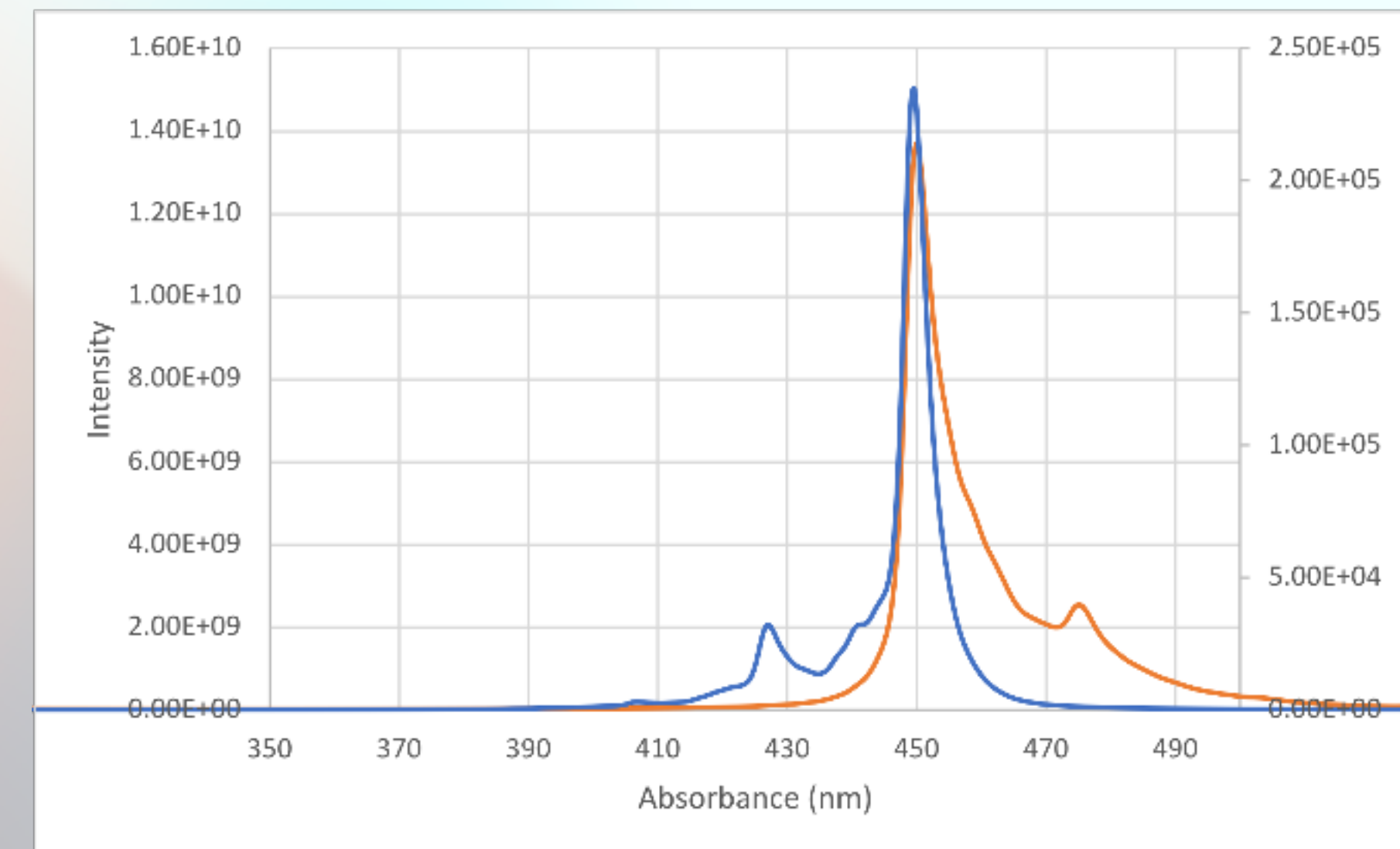


Excited states

Vertical transition model



Vertical transitions only



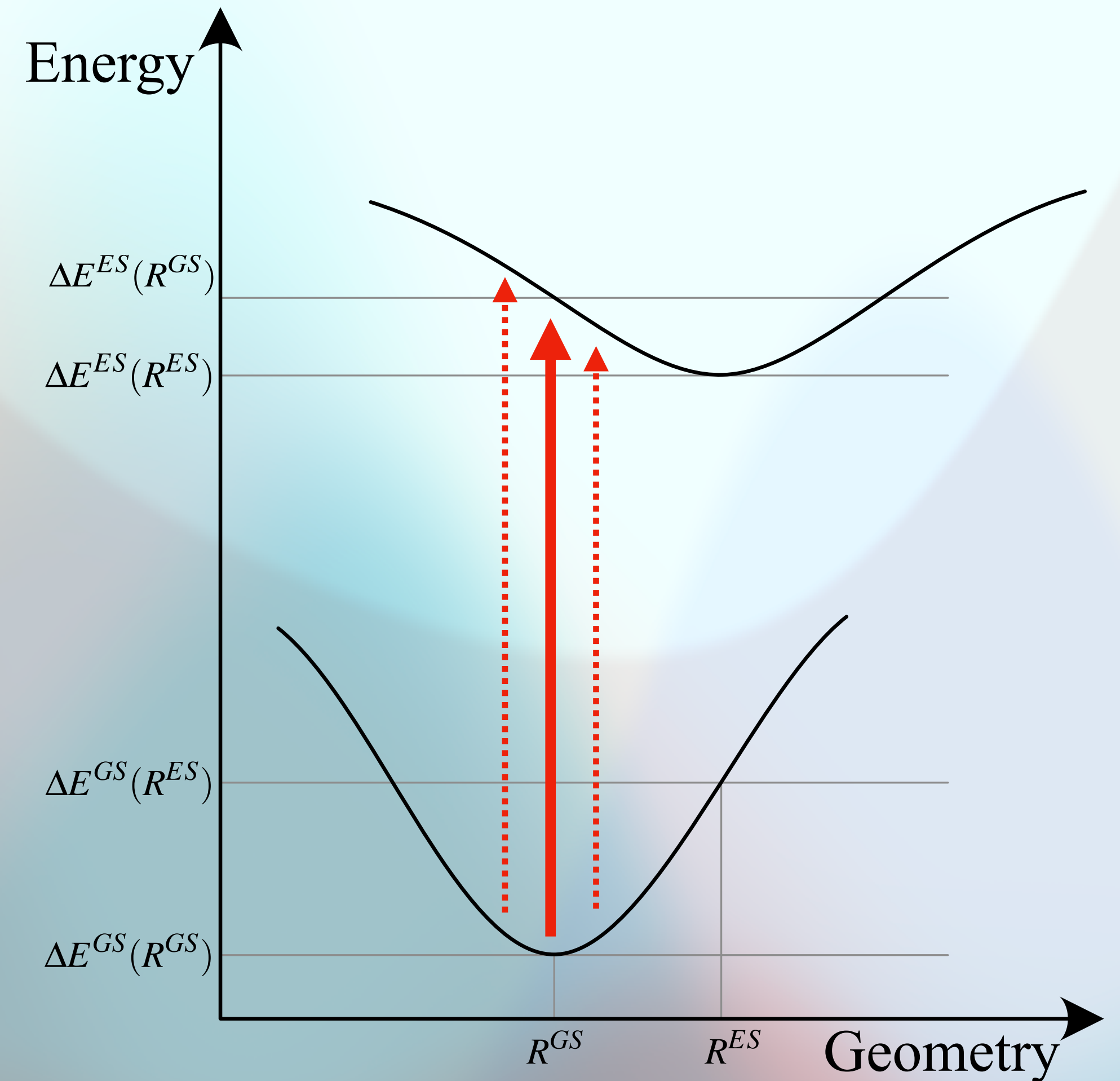
Full excited state dynamics

**these are from different fluorophores*

Excited states

Vertical transition model

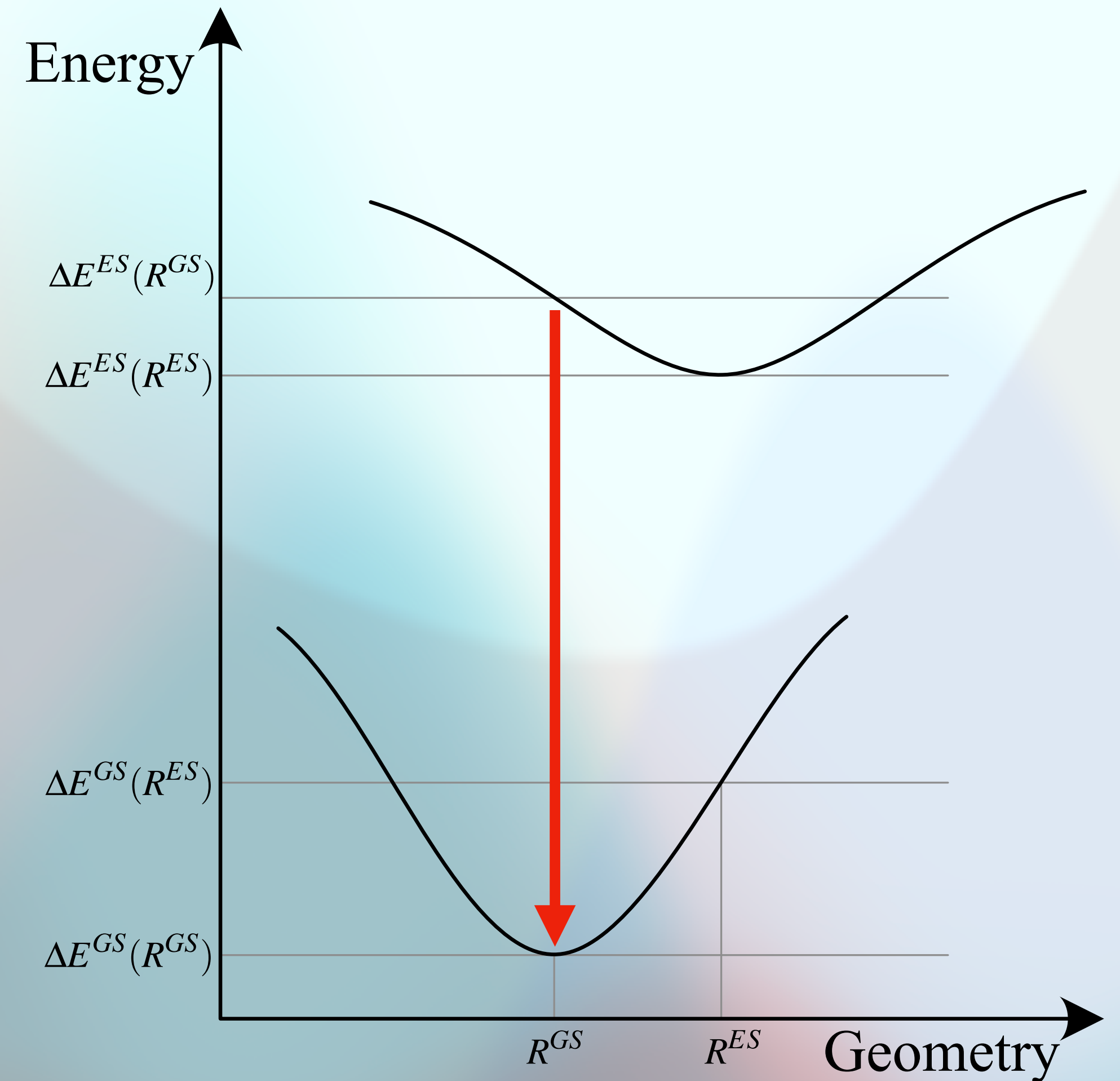
1. A vertical transition will occur from some point on the GS PES to the ES. The variation in the placement on the PES gives rise to broad peaks



Excited states

Vertical transition model

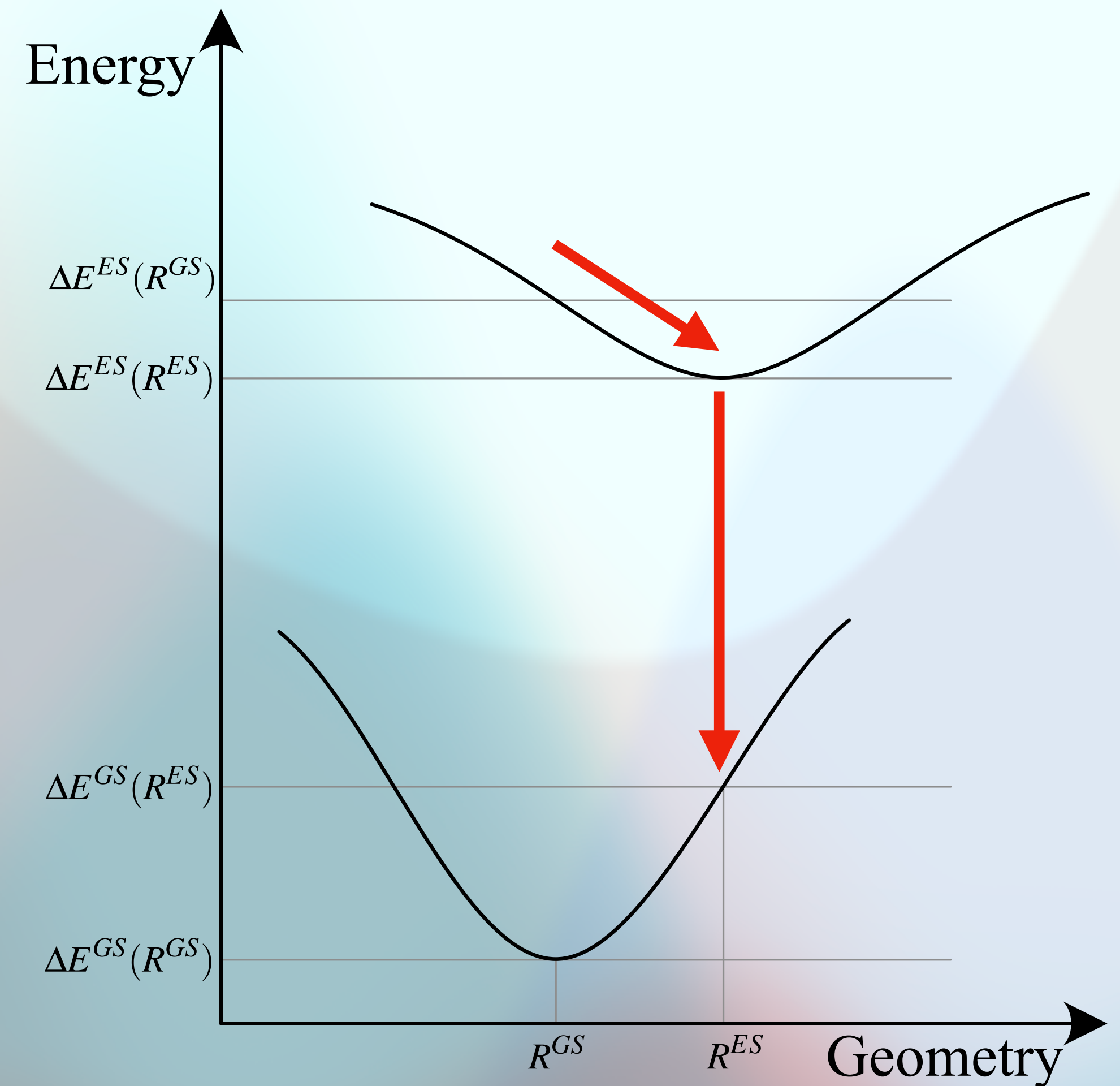
1. A vertical transition will occur from some point on the GS PES to the ES. The variation in the placement on the PES gives rise to broad peaks
2. If the ES is short lived, the structure might not have time to relax and will emit a photon straight away (how boring)



Excited states

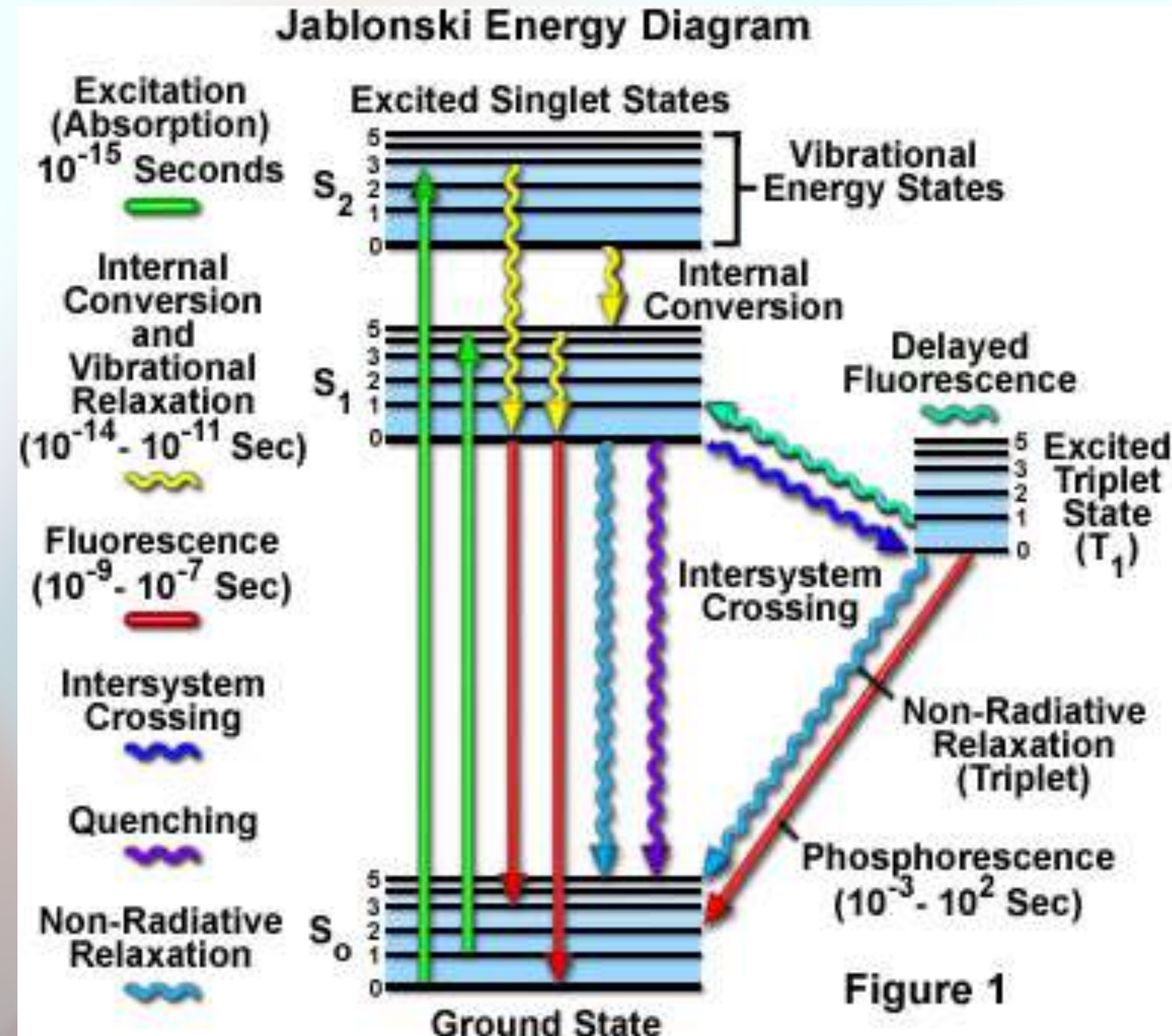
Vertical transition model

1. A vertical transition will occur from some point on the GS PES to the ES. The variation in the placement on the PES gives rise to broad peaks
2. If the ES is short lived, the structure might not have time to relax and will emit a photon straight away (how boring)
3. If the ES is long lived, the solvent and solute will have time to relax before emitting, usually emitting a lower energy photon in the process.



Excited states

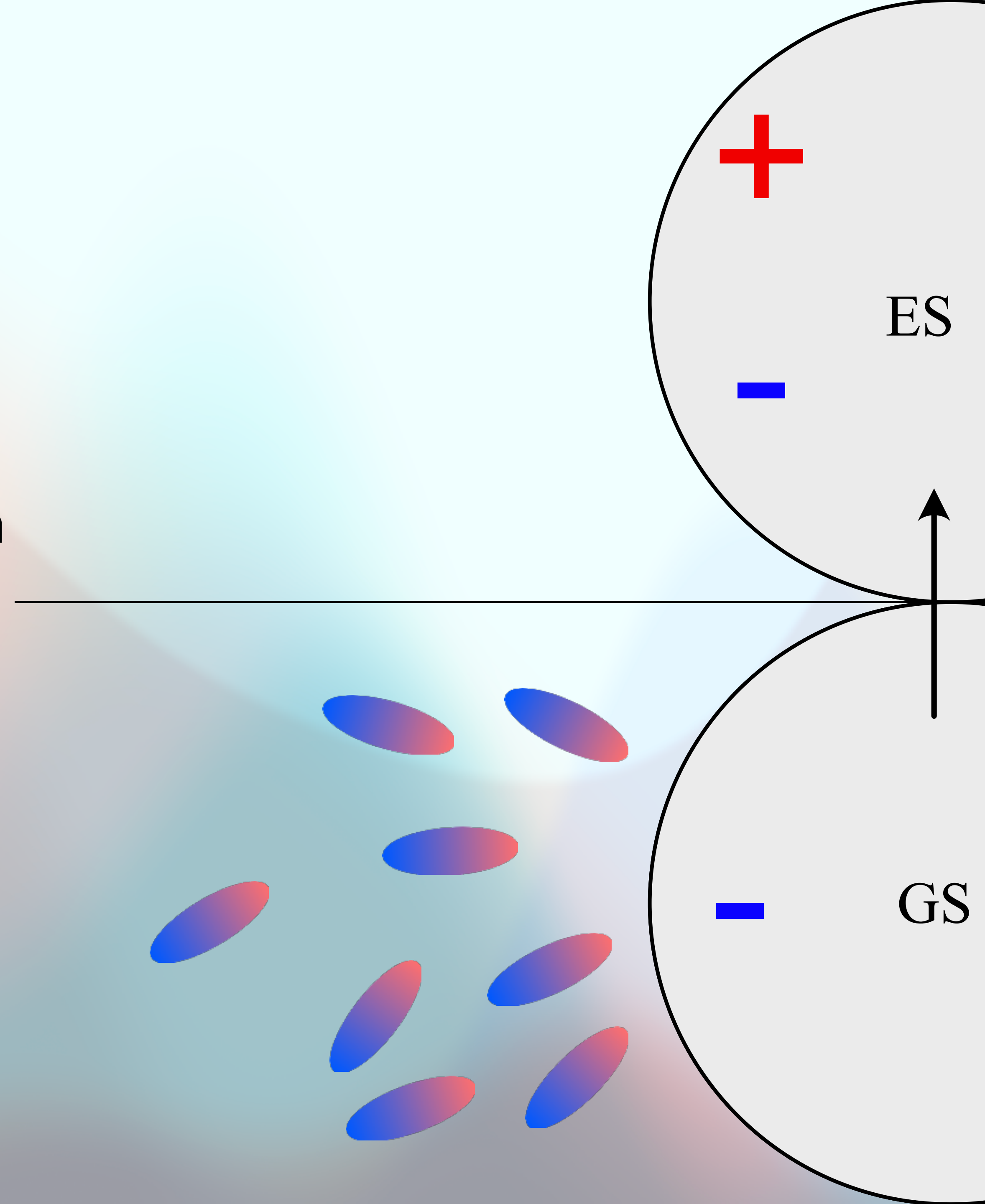
Vertical transition model



Excited states

Equilibrium

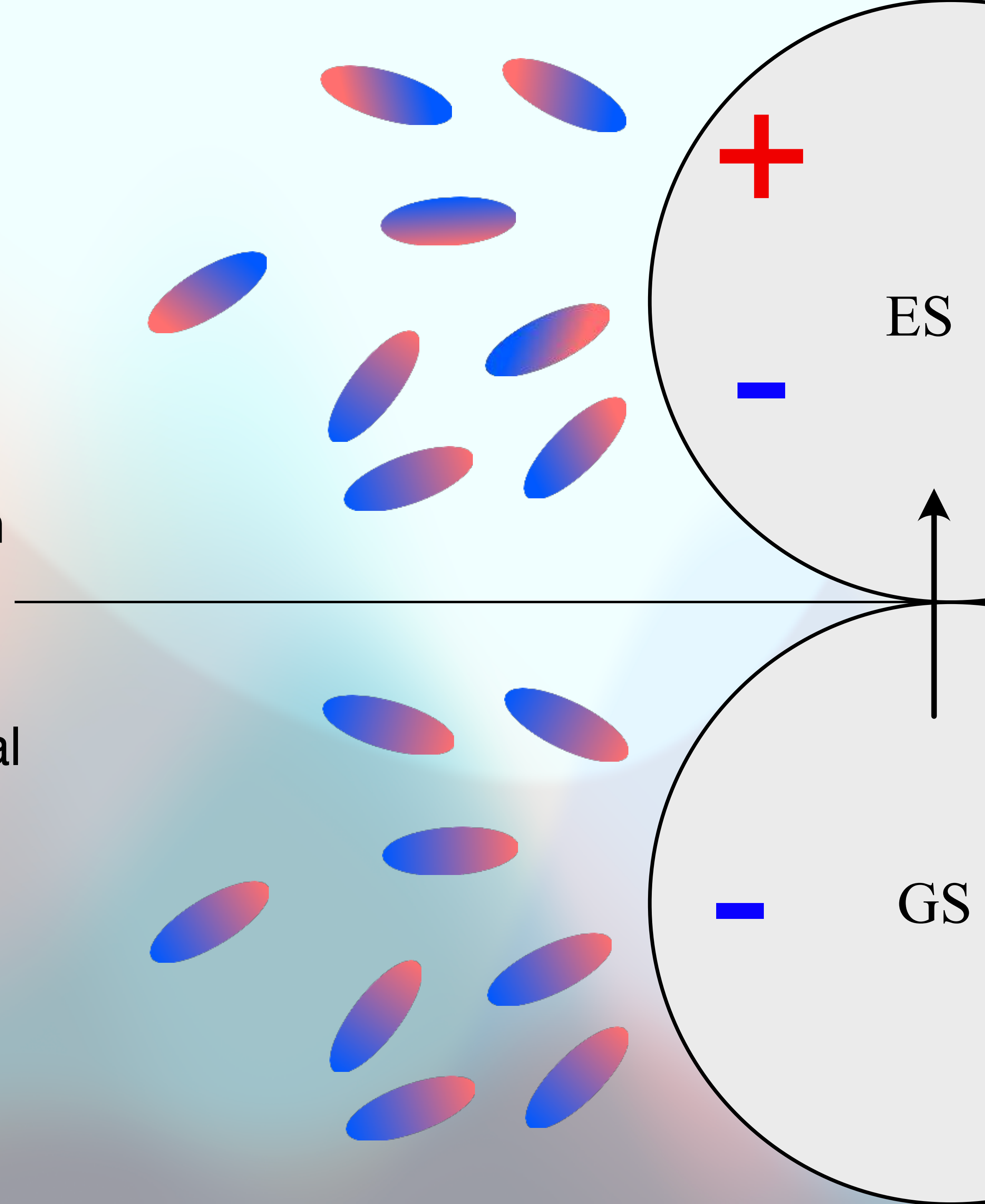
- This relaxation process gives rise to a particular feature of ES solvation - the solvent itself has two ways in which it can stabilise the solute wrt the GS



Excited states

Equilibrium

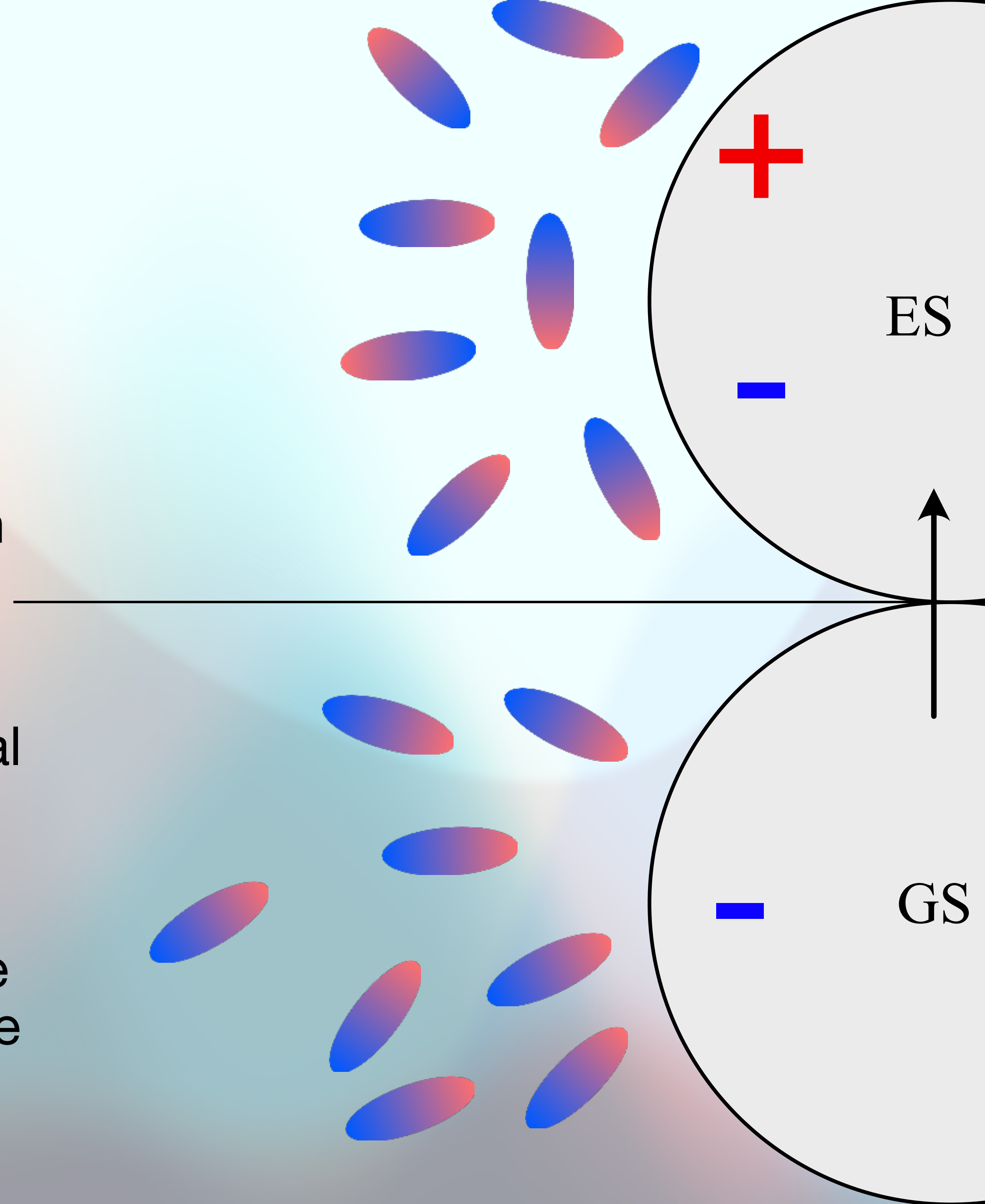
- This relaxation process gives rise to a particular feature of ES solvation - the solvent itself has two ways in which it can stabilise the solute wrt the GS
 1. Fast transition - The solvent gets polarised by the near-instant electrical transition of the solute, but can't re-orient itself in space in this timeframe



Excited states

Equilibrium

- This relaxation process gives rise to a particular feature of ES solvation - the solvent itself has two ways in which it can stabilise the solute wrt the GS
 1. Fast transition - The solvent gets polarised by the near-instant electrical transition of the solute, but can't re-orient itself in space in this timeframe
 2. Slow transition - The solvent has time to re-orient itself to better stabilise the solute



Excited states

Equilibrium

- The terminology around these is where it starts to get confusing
- Equilibrium Solvation - the fast and slow responses are in equilibrium **with each other**
- Non-equilibrium Solvation - the fast and slow responses are **not** in equilibrium **with each other**

Excited states

Equilibrium - Partitioning the surface charges

- Naturally, this means that we have to partition the electrostatic response into fast and slow components.
- Multiple ways to do this, most look something like this:
 1. Separate fast and slow component of the GS surface charges
 2. Polarise **the fast** component wrt to the ES of interest
 3. Sum the respective GS slow and ES fast charges together

- ϵ_0 = solvent dielectric constant
- ϵ_∞ = optical dielectric constant (n^2)
- σ = surface charges

$$\sigma^f = \left(\frac{\epsilon_\infty - 1}{\epsilon_0 - 1} \right) \sigma$$

$$\sigma^s = \left(\frac{\epsilon_0 - \epsilon_\infty}{\epsilon_0 - 1} \right) \sigma$$

Excited states

Equilibrium - Partitioning the surface charges

$$\chi^f = \left(\frac{\varepsilon_\infty - 1}{\varepsilon_0 - 1} \right)$$

$$\chi^s = \left(\frac{\varepsilon_0 - \varepsilon_\infty}{\varepsilon_0 - 1} \right)$$

- Hexane:

- $\varepsilon_0 = 1.88$

- $\varepsilon_\infty = 1.89$

- $\chi_f = 1.01$

- $\chi_s = -0.01$

- Ethanol:

- $\varepsilon_0 = 24.85$

- $\varepsilon_\infty = 1.85$

- $\chi_f = 0.04$

- $\chi_s = 0.96$

- Water:

- $\varepsilon_0 = 78.4$

- $\varepsilon_\infty = 1.78$

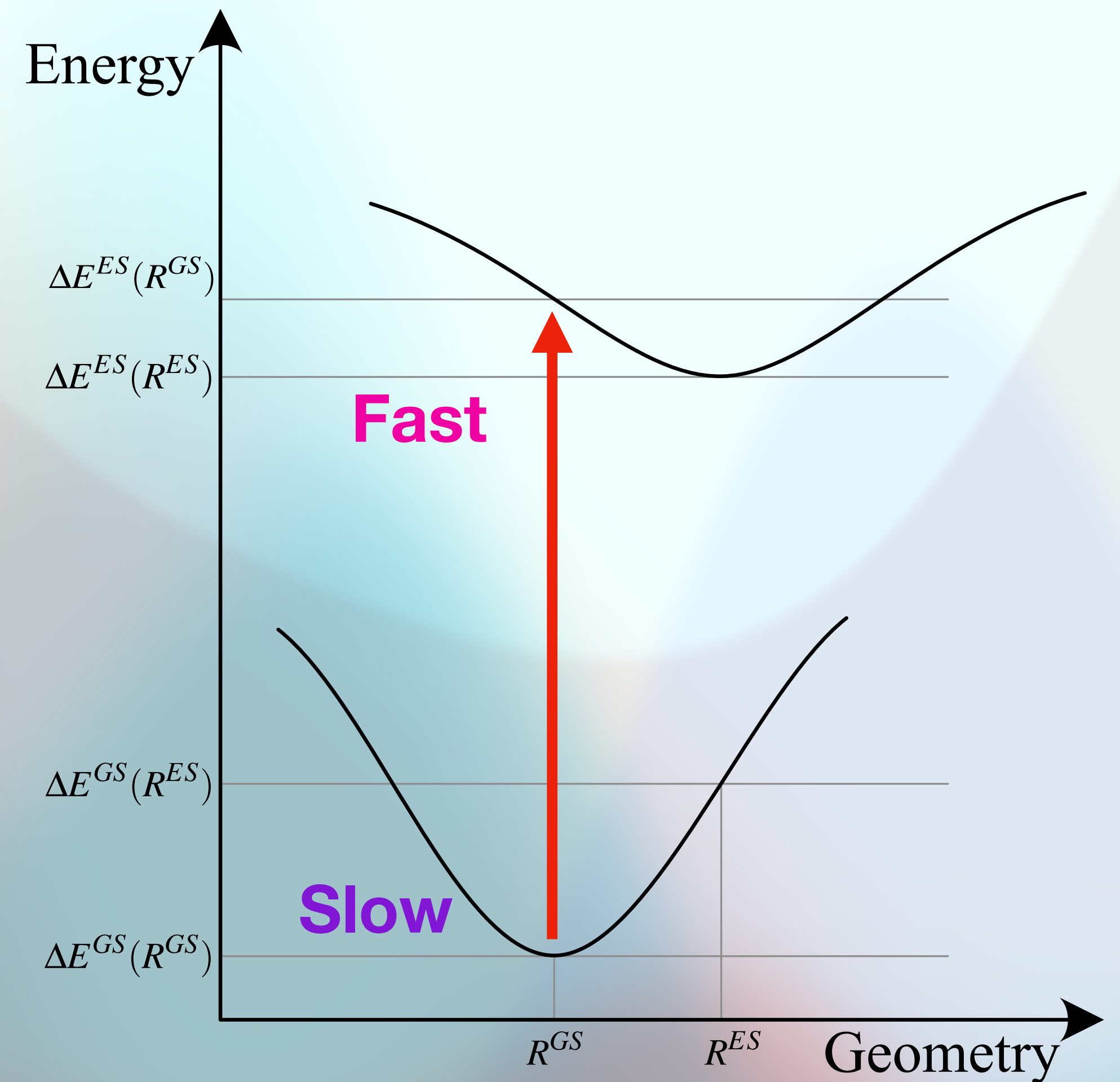
- $\chi_f = 0.01$

- $\chi_s = 0.99$

Excited states

Equilibrium

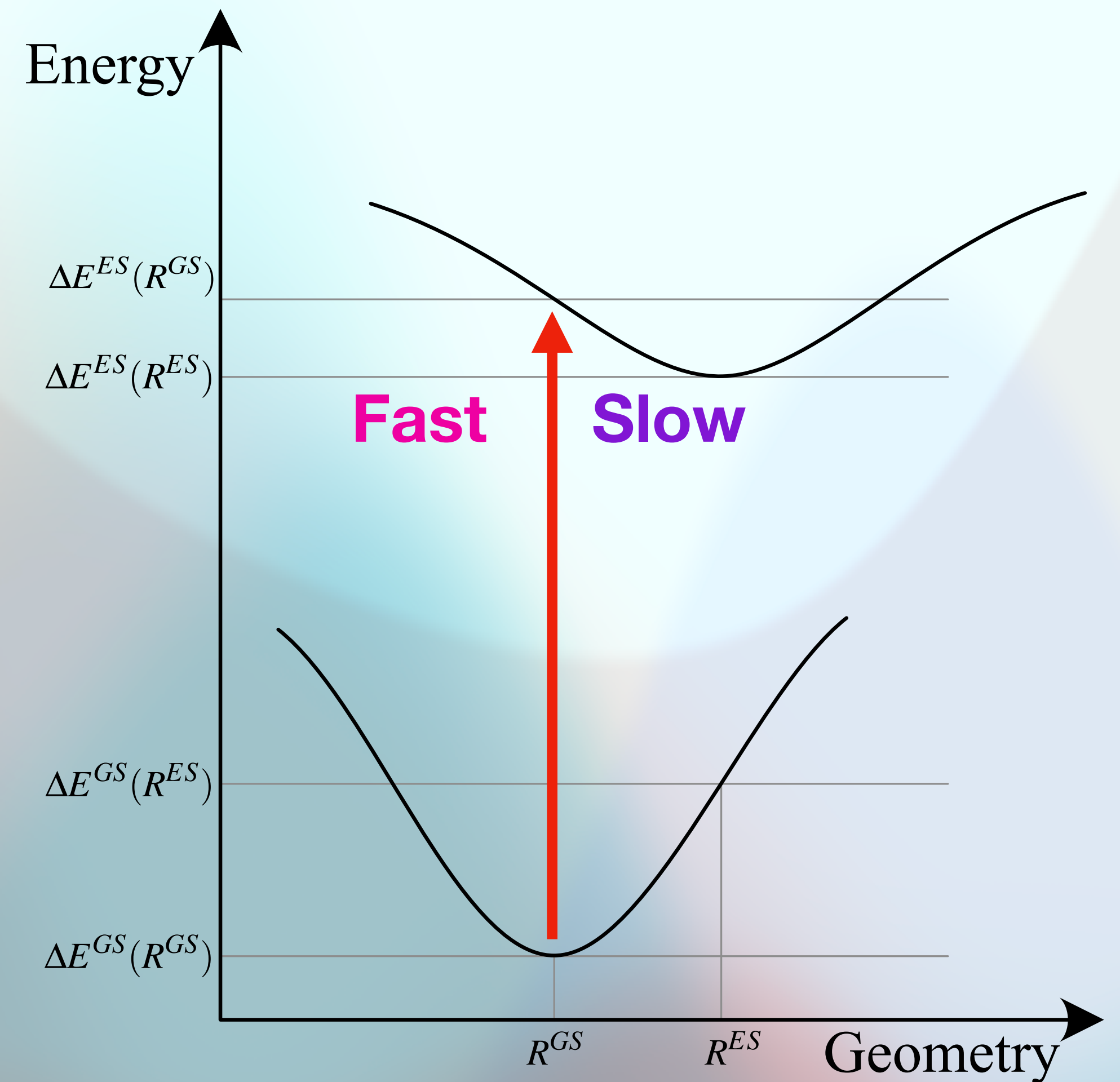
- The consequence of this equilibrium definition is four different conditions
 1. GS-VT calculation, Solvent in non-eq



Excited states

Equilibrium

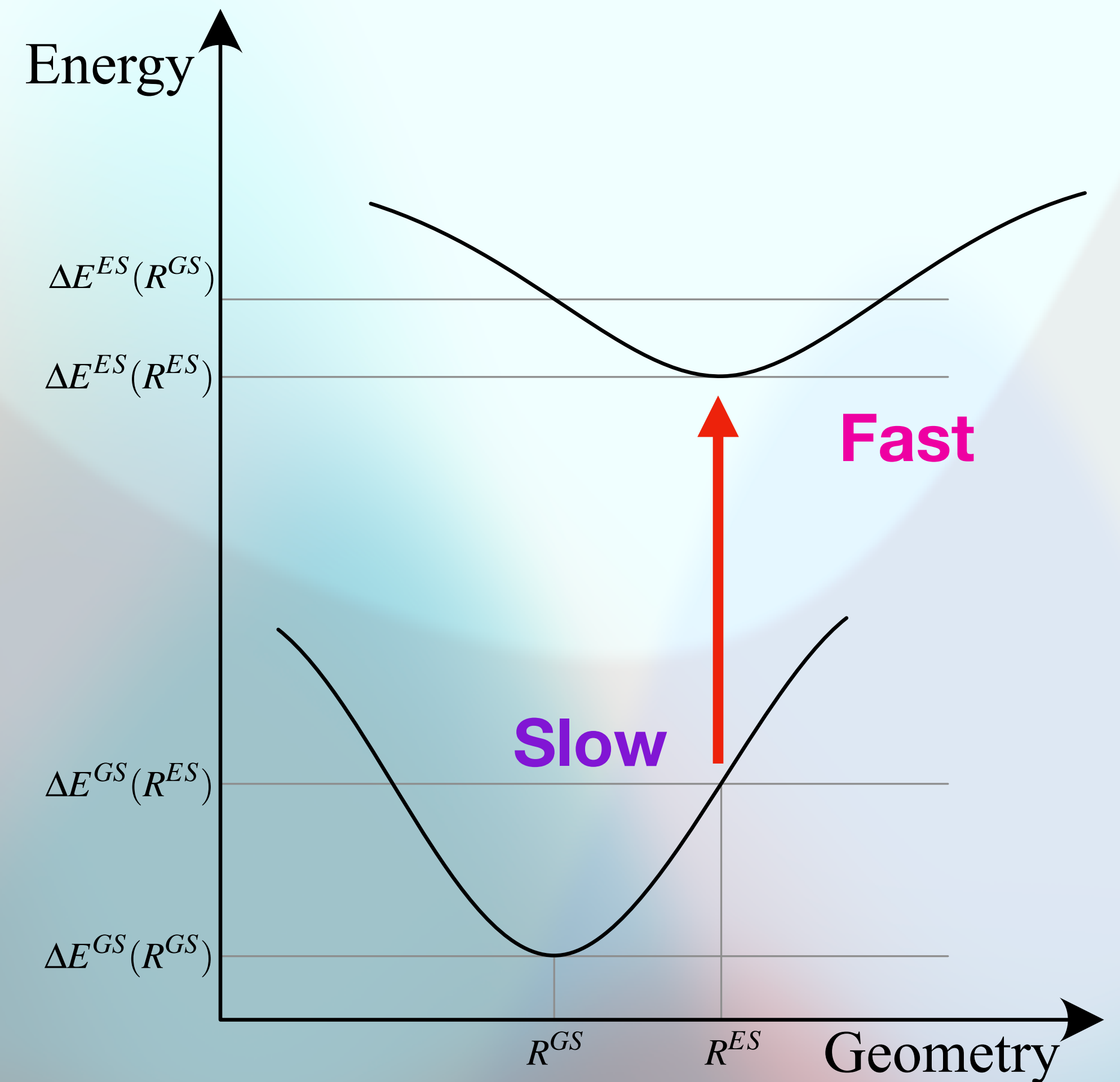
- The consequence of this equilibrium definition is four different conditions
 1. GS-VT calculation, Solvent in non-eq
 2. GS-VT calculation, Solvent in eq



Excited states

Equilibrium

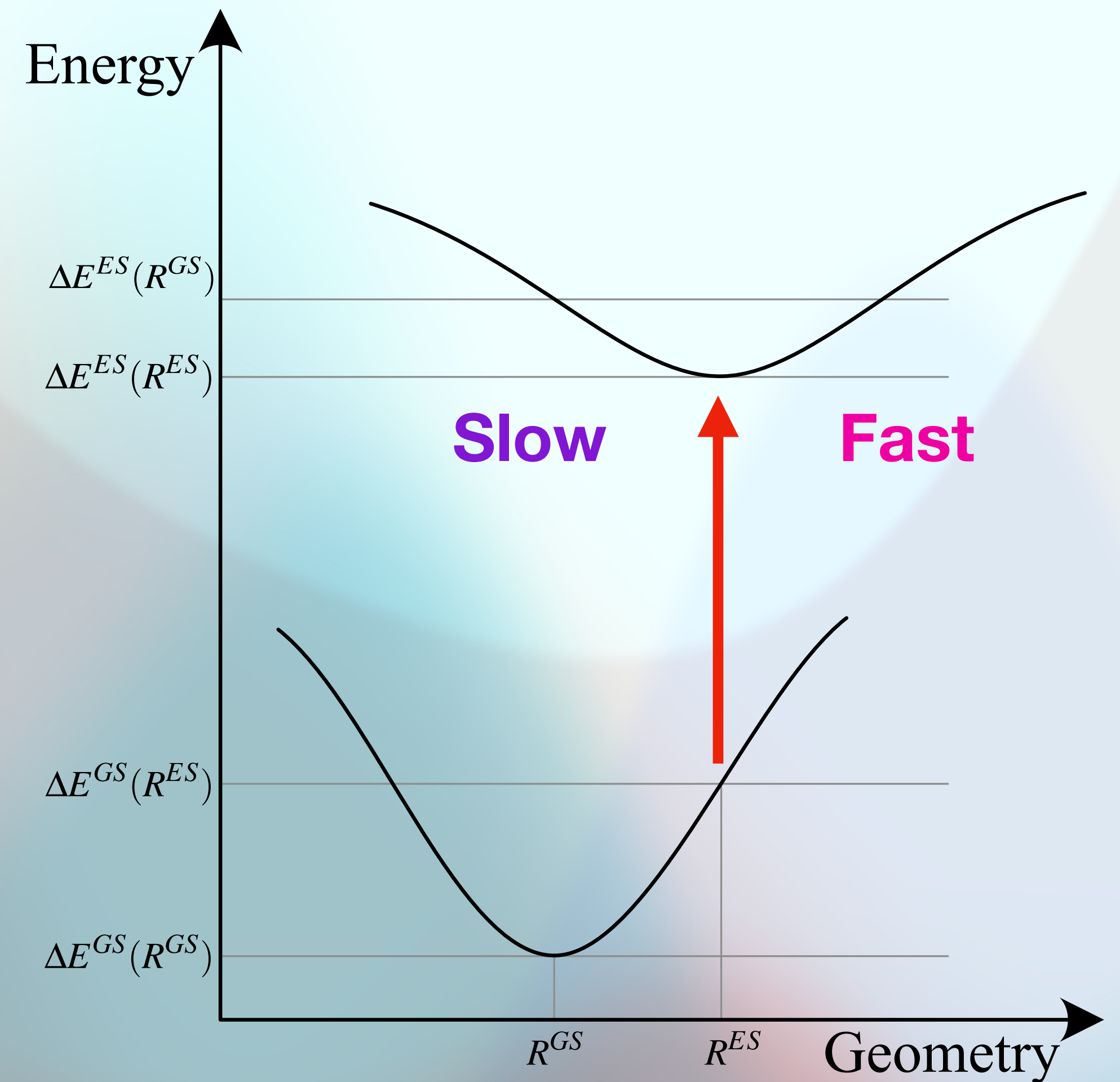
- The consequence of this equilibrium definition is four different conditions
 1. GS-VT calculation, Solvent in non-eq
 2. GS-VT calculation, Solvent in eq
 3. ES-VT calculation, Solvent in non-eq



Excited states

Equilibrium

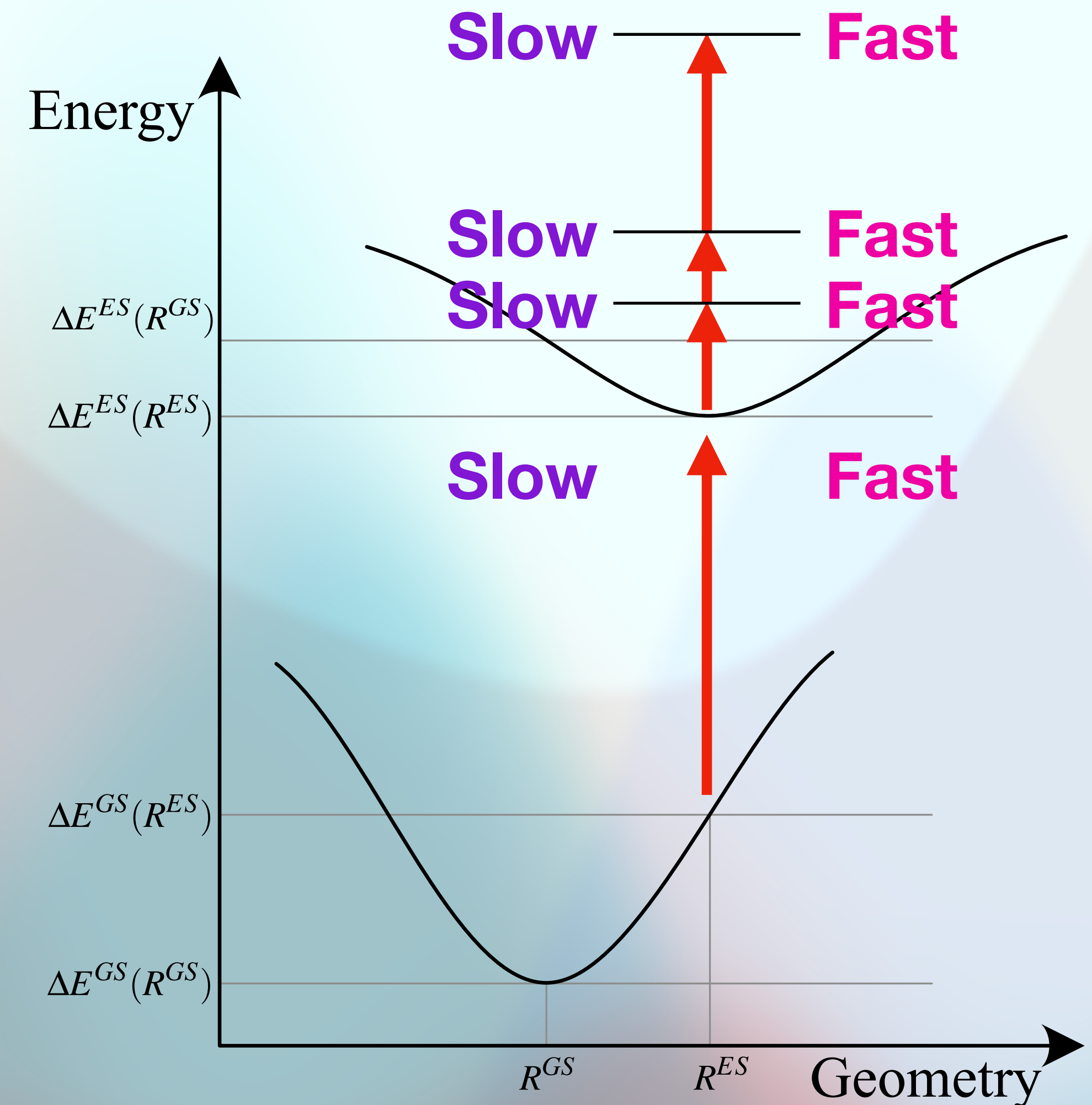
- The consequence of this equilibrium definition is four different conditions
 1. GS-VT calculation, Solvent in non-eq
 2. GS-VT calculation, Solvent in eq
 3. ES-VT calculation, Solvent in non-eq
 4. ES-VT calculation, Solvent in eq



Excited states

Equilibrium

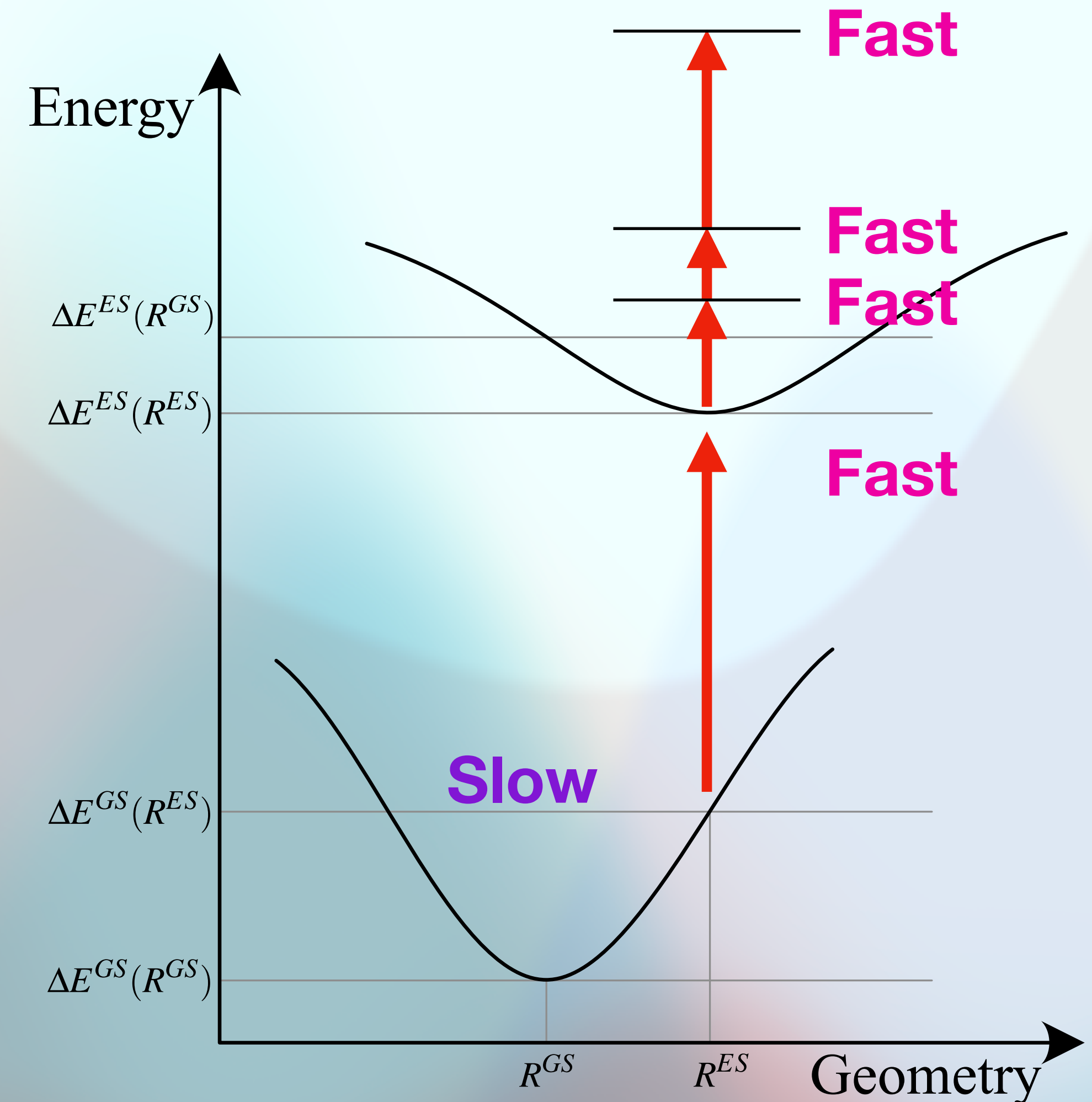
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 4. ES-VT calculation, Solvent in eq



Excited states

Equilibrium

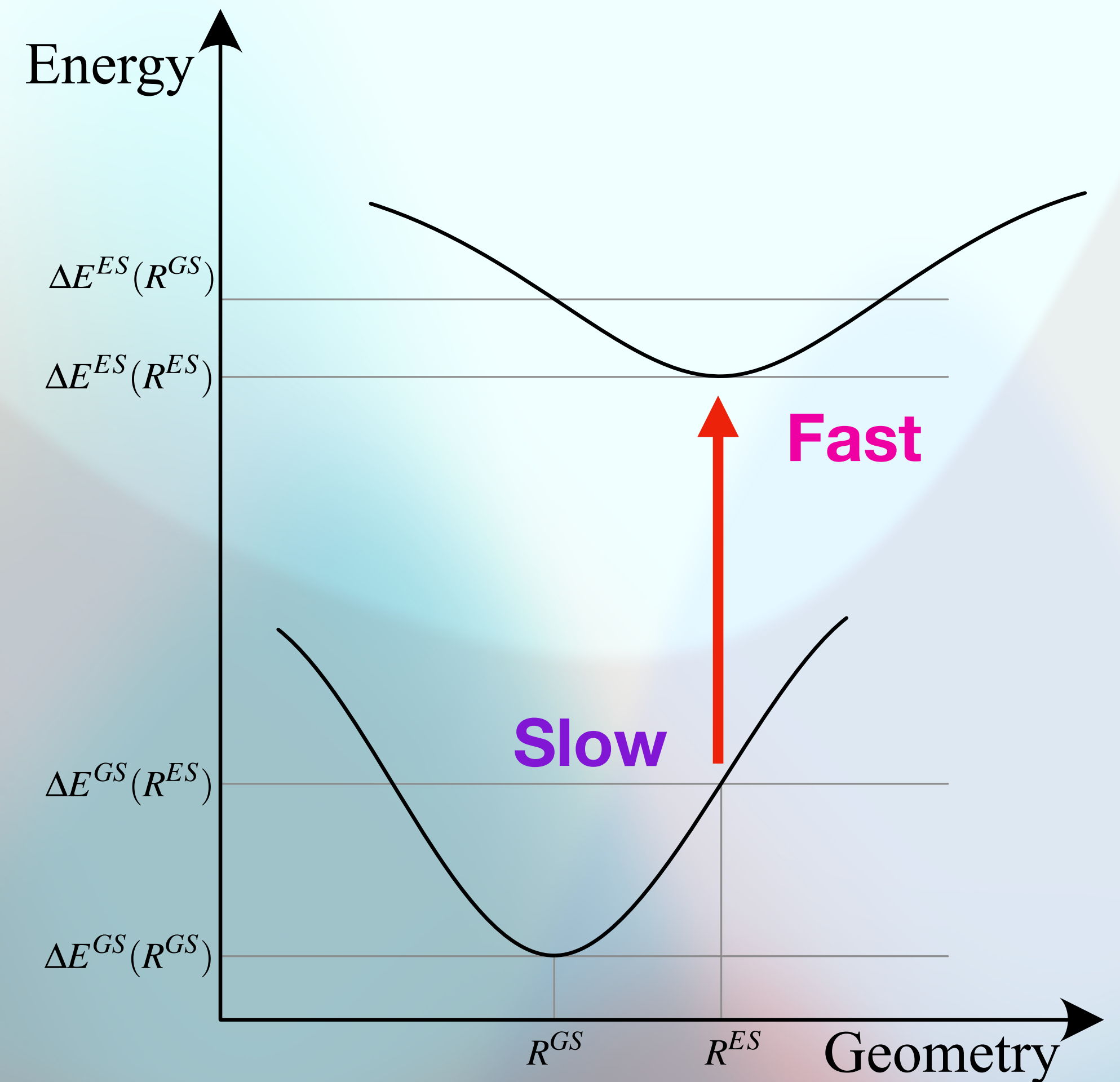
- The consequence of this equilibrium definition is four different conditions
 1. GS-VT calculation, Solvent in non-eq
 2. GS-VT calculation, Solvent in eq
 3. ES-VT calculation, Solvent in non-eq
 4. ES-VT calculation, Solvent in eq



Excited states

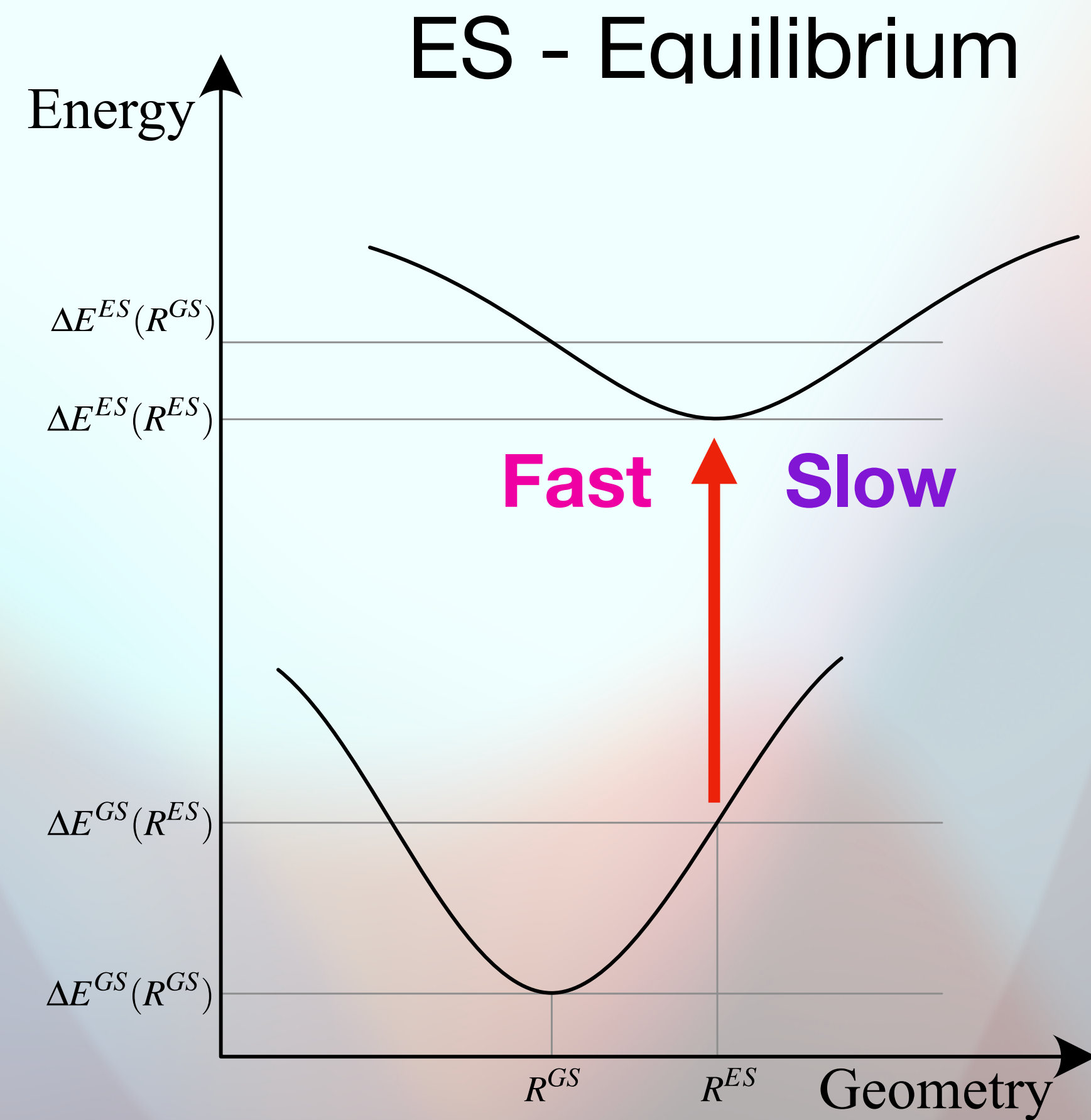
Equilibrium

- The consequence of this equilibrium definition is four different conditions
 1. ES-ES calculation, Solvent in eq
 2. ES-ES calculation, Solvent in non-eq
 3. ES-VT calculation, Solvent in non-eq
- We **cannot polarise the slow charges** of the ES directly



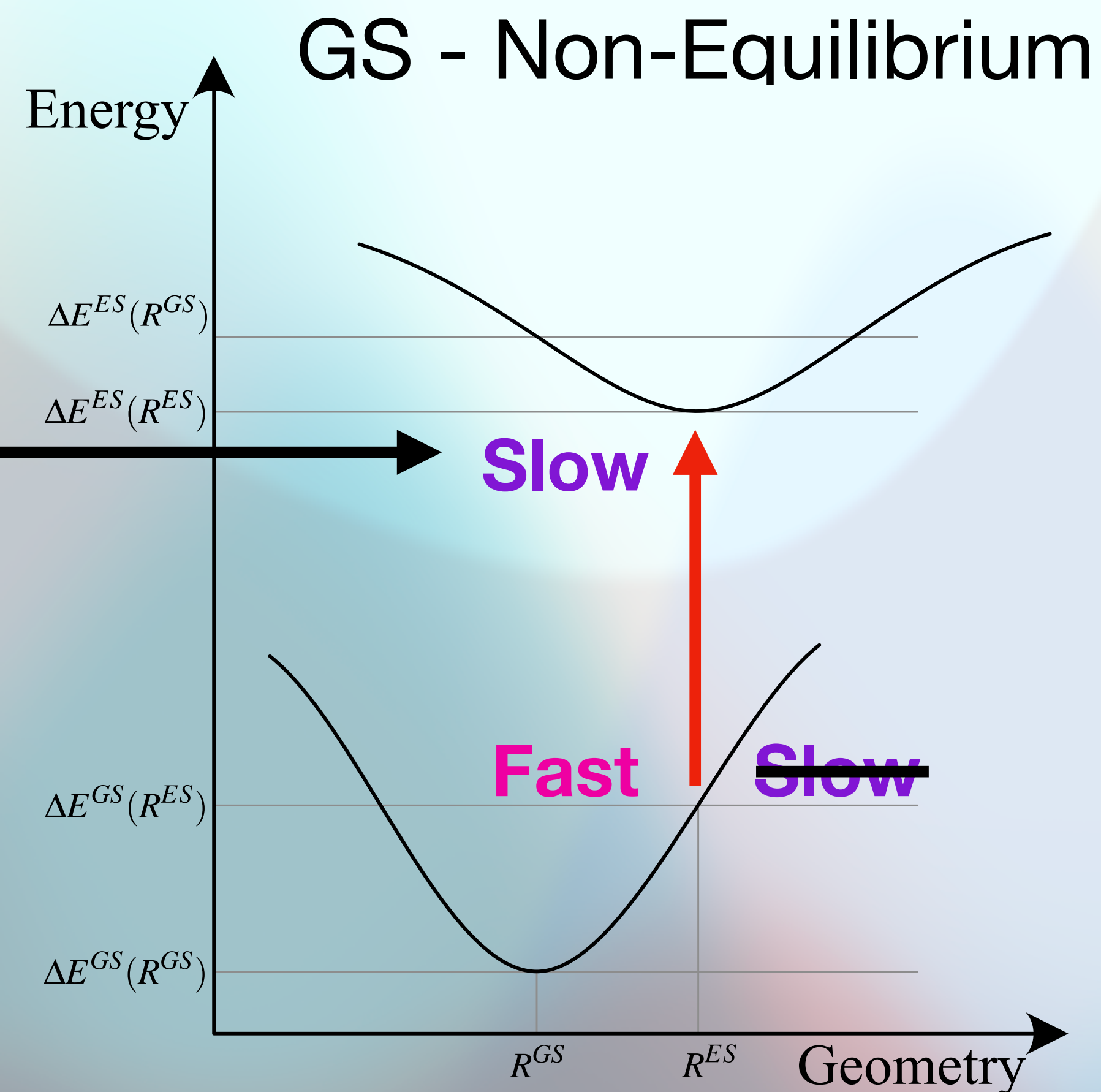
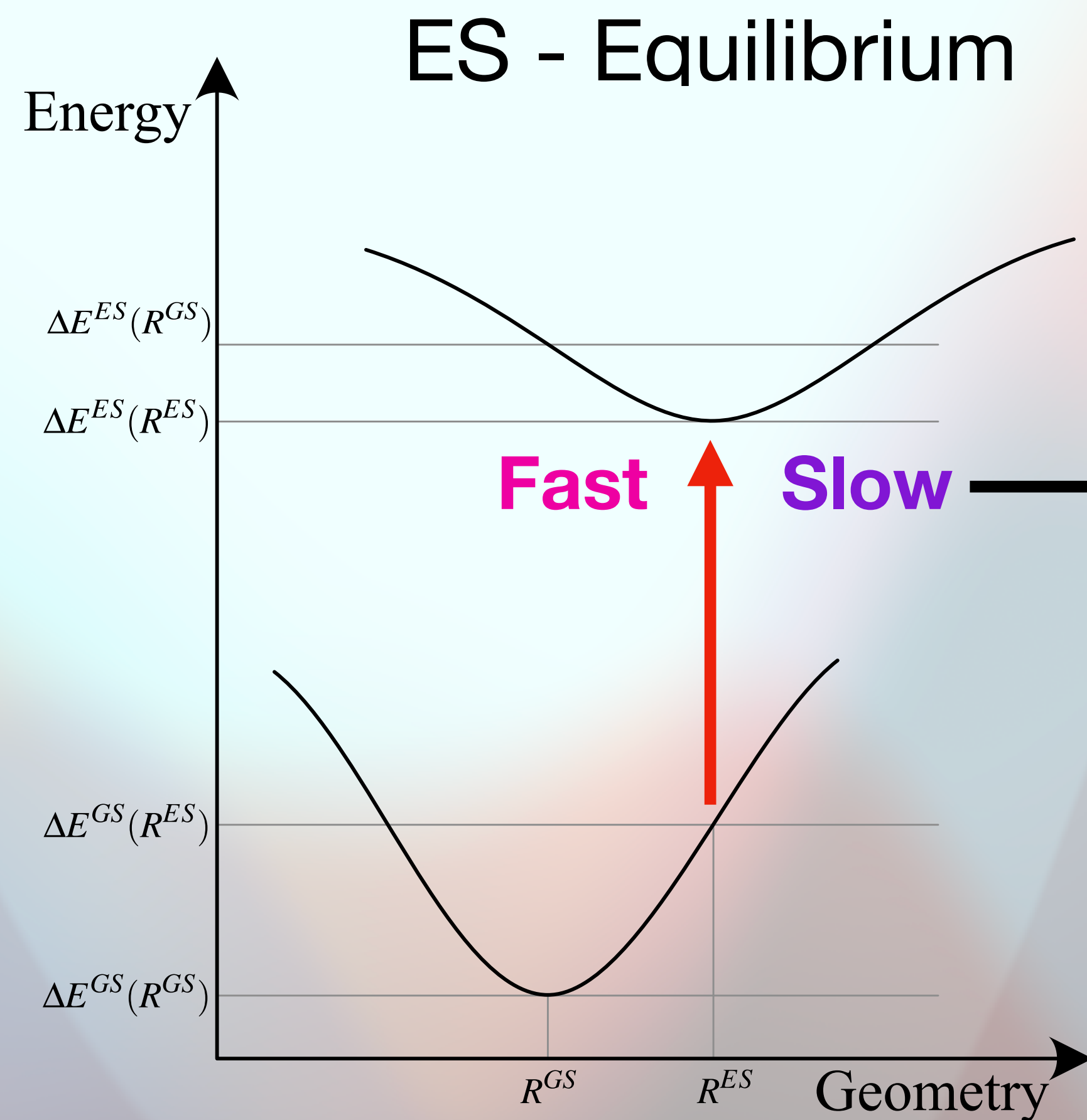
Excited states

Emission



Excited states

Emission



Equilibrium vs non-equilibrium

My recommendation

- Equilibrium should always be used when optimising for an excited state
- Non-equilibrium should be used for vertical transitions
- Emission is a very specific tool and requires specific programs
 - Gaussian can do it, but it's clunky to chain jobs together
 - Q-Chem can do it, in a relatively easy manner, but it's REALLY poorly documented
 - NWChem does it easily, as a part of `do_cosmo_vem 2`, but otherwise can't seem to.

State Specific vs Linear Response

AKA, The point where my brain gives up on all the crossover in terminology

AKA, The point where the slides get verbose 😅

I apologise in advance if I lose any of you here... I promise I'll record and upload this for people to go back to!

SS vs LR

Linear Response

- Linear response solvation (LR) at its core uses the **transition density** to calculate the solvent response to the excitation.
- This is a product of the (LR) TD-DFT calculation, and comes from the transition multipole moment, which means that **it disappears for non-optically allowed transitions**
 - The solvent response in turn will be much smaller than expected in these cases
- This presents larger issues for situations where large electronic rearrangements happen, since there will be less of an orbital overlap between the states (e.g. CT states, Rydberg states)

SS vs LR

State Specific

- State-specific theory instead uses:
 - The density of the reference state $\rho_0(r)$ to calculate the **slow** charges
 - density difference between the ground and excited state to calculate the **fast** charges $\Delta\rho_n(r) = \rho_n(r) - \rho_0(r)$
- Practically speaking, this is computed by partitioning the **reference** state surface charges and re-polarising them in the presence of the transition state

When reading the literature, I constantly confused state-specific with equilibrium, as one might naturally do, given the name...

SS vs LR

State Specific

$$\sigma_0^f = \left(\frac{\epsilon_\infty - 1}{\epsilon_s - 1} \right) \sigma_0$$

$$\sigma_0^s = \left(\frac{\epsilon_s - \epsilon_\infty}{\epsilon_s - 1} \right) \sigma_0$$

- To break this down further:
 1. Take the ground state density ρ_0 to calculate the respective surface charges σ_0
 2. Partition the surface charges using some partition function to get the fast σ_0^f and slow σ_0^s partitions of the charges
 3. Perturb the fast component with the state specific density difference σ_n^f
 4. Recombine them to get the non-equilibrium charges $\sigma_{0 \rightarrow n}^{neq} = \sigma_0^s + \sigma_n^f$
- This is usually performed in one job

SS vs LR

State Specific

$$\sigma_0^f = \left(\frac{\epsilon_\infty - 1}{\epsilon_s - 1} \right) \sigma_0$$

$$\sigma_0^s = \left(\frac{\epsilon_s - \epsilon_\infty}{\epsilon_s - 1} \right) \sigma_0$$

- For emission:
 1. Perform an equilibrium excited state calculation, polarising the charges against the excited state density. Gives σ_n
 2. Partition the charges to get the fast σ_n^f and slow σ_n^s components
 3. Perform a ground state non-equilibrium calculation (forces the partitioning of charges) to get $\sigma_0^s + \sigma_n^f$
 4. Recombine them to get the non-equilibrium charges $\sigma_{n \rightarrow 0}^{neq} = \sigma_n^s + \sigma_0^f$
- This typically requires two separate jobs to do properly. Some packages will chain these automagically.

LR Solvation

My recommendation

- Linear Response solvation is implemented in pretty much everything since it comes for free with the vertical excitation calculation
- If you don't specify what you're going to do in a program, it will either complain at you, or probably use LR solvation
- SS solvation **is not** implemented in most packages, and in packages where it's not, most documentation is VERY ambiguous as to how it's handling the excitation
- Every package that does LR solvation will allow you to choose equilibrium or non-equilibrium

LR Solvation and Equilibrium

My recommendation

- This also means that LR solvation can be used to calculate transitions **between** states as well.
- Remember that vertical transitions are a projection from the ground state to a higher state, so any errors will be propagated and exacerbated.
- The best LR methods have errors of anywhere up to 0.8 eV (in my benchmarking)

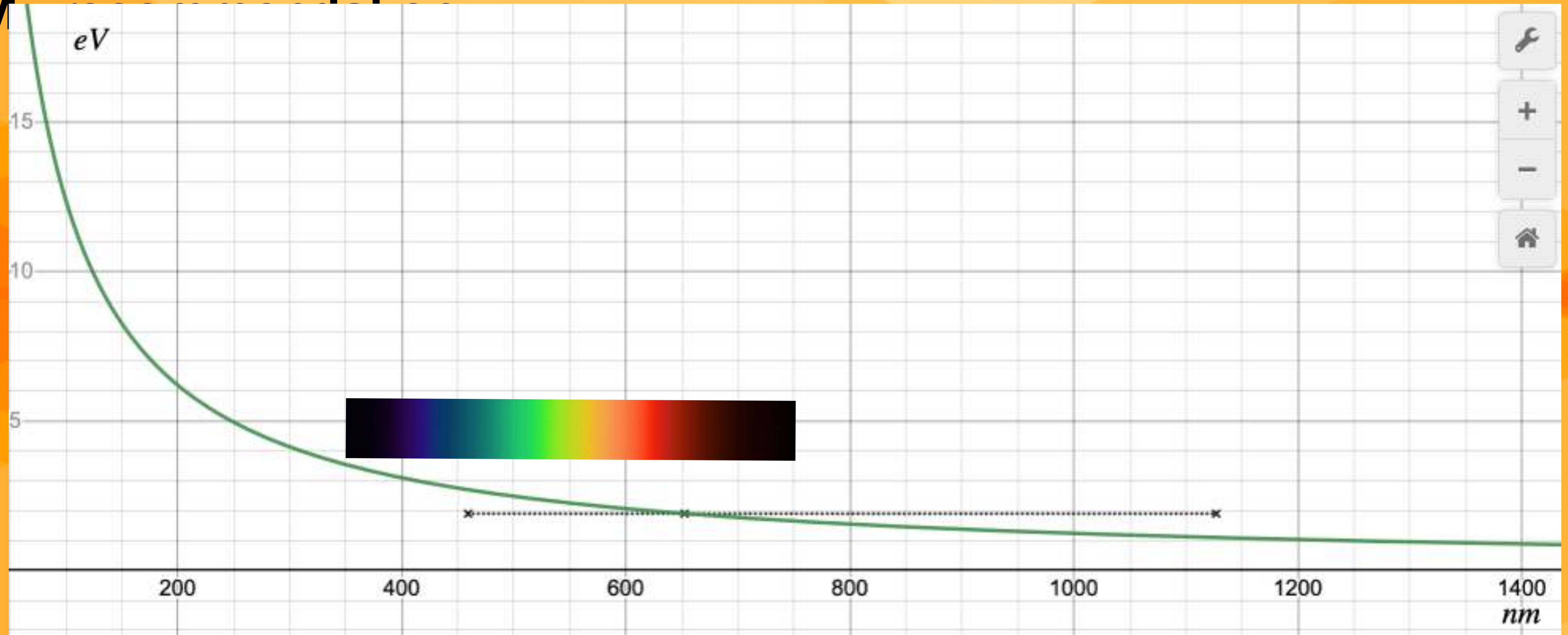
LR Solvation and Equilibrium

M

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SS vs LR

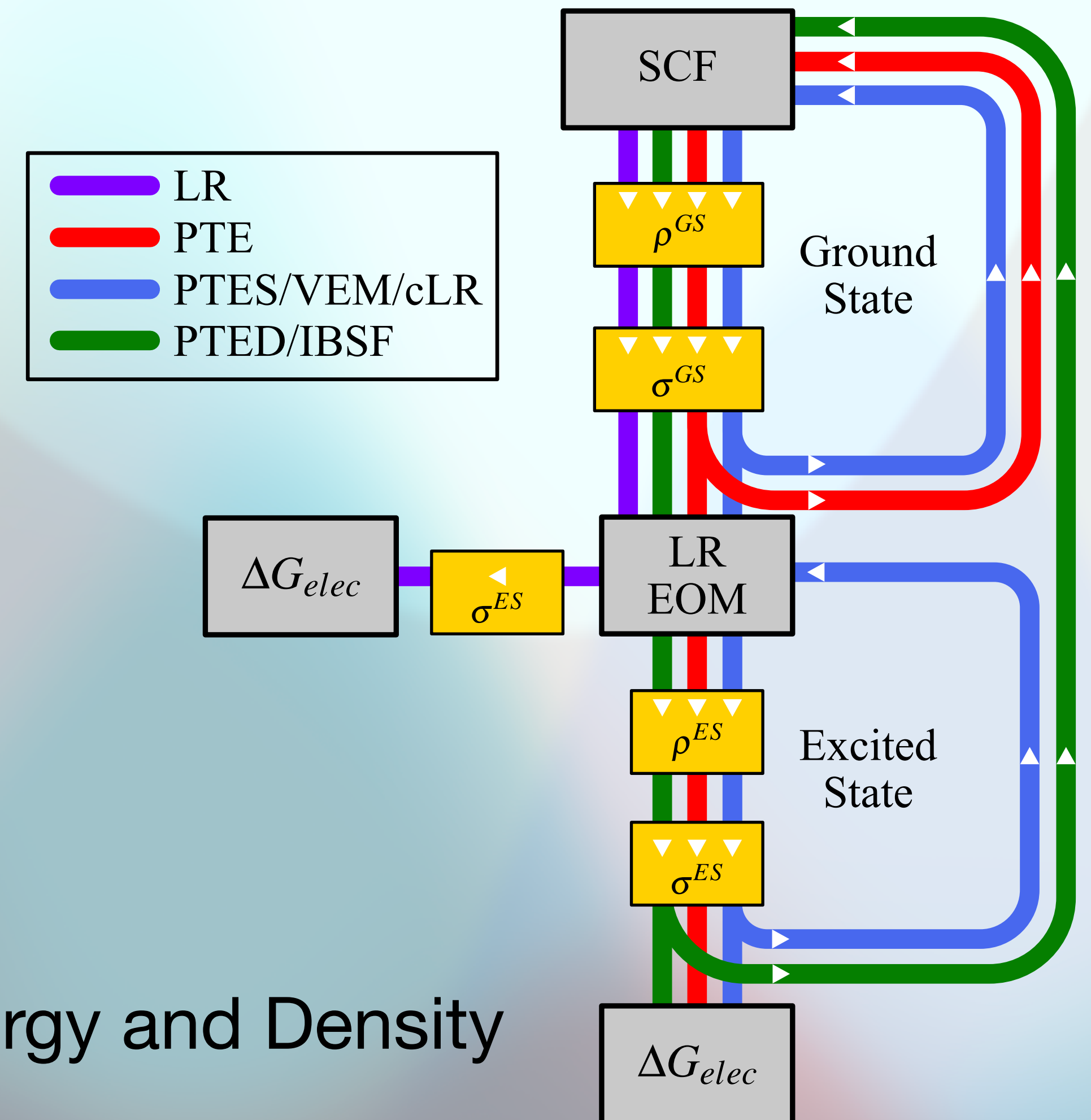
Why this gets more confusing to study

- State specific approaches can be considered an extension, or correction to the linear response solvation approach, so the first SS implementation was called “corrected-LR” (cLR).
 - The name has stuck despite SS being a distinctly separate approach to LR
- Other SS approaches come with more interesting names, like “Vertical Excitation Model” (VEM) which make it even more confusing, when you go to google “*vertical excitation models*”
- When looking deeper, these models get even more confusing when you get into the territory of self-consistency WITH excited states

Simplifying all these approaches

The “Perturbation to...” model for excited states

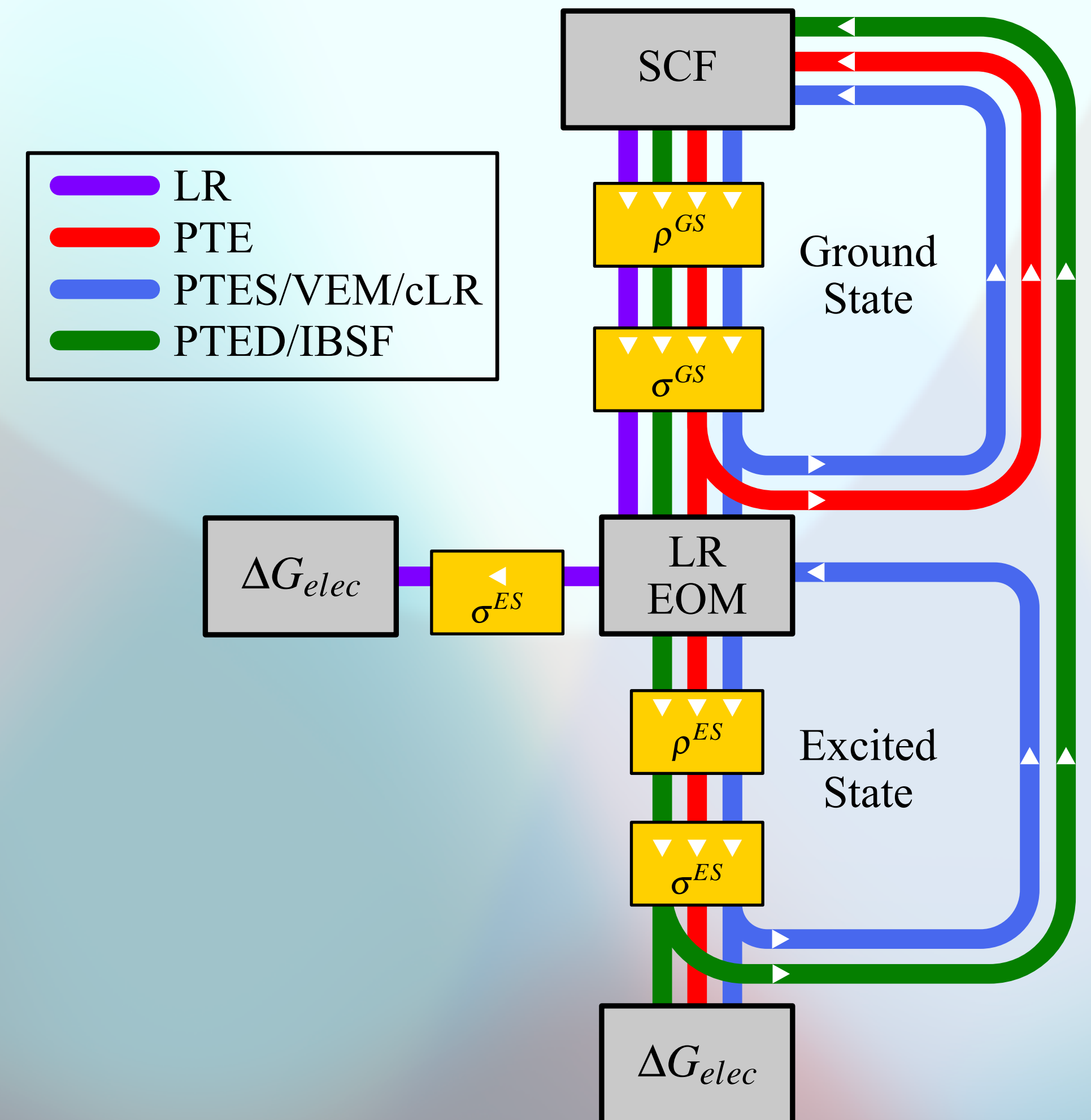
- One way to look at these approaches is to consider their self consistency in relation to ground state, or excited state, similarly to how we can treat correlated method solvation
- PTx notation is about Perturbation To...
 - PTE - Perturbation to Energy
 - PTES - Perturbation to Excited State
 - PTED - Perturbation with self consistent Energy and Density



Simplifying all these approaches

Equivalence

- Under this model, we have some terms that become equivalent in the framework of TD-DFT
 - PTES = Vertical Excitation Model (VEM)
 - cLR = First iteration of PTES
 - PTED = Improta, Barone, Scalman, Frisch (IBSF)



Electrostatic terms

My recommendation

- This is tricky, and VERY case specific, but also, watch this space...
- cLR and VEM seem to be the best approaches.
- Papers suggest that IBSF/PTED are non-variational and change the ground state orbitals too much for the TD-DFT calculation to still be meaningful.
- For analytical gradients this becomes even trickier, since a lot of these methods are post-hoc corrections.
 - SMD for ground state opts still
 - For excited state opts, cLR seems to be better than LR only in some cases, and is much more expensive

Non-Electrostatic Terms (Excited State)

AKA, The point where we need more work

Non-electrostatic terms

- Simply put, this is the point where we don't have many good options
 - Ground state dispersion corrections are not appropriate for the excited state
 - Ground state non-electrostatic terms are not appropriate for the excited state
 - There can be very large differences between the ground and excited state in both geometry, and non-electrostatic solvation considerations

Non-electrostatic terms

SMSSP

- This is the best method we have so far
- Since dispersion comes from the C^6 term, which comes from α
 - Technically the frequency dependent polarisability $\alpha(\omega)$, which means LR theory breaks down here...
- Truhlar, Cramer and co. extended SMD to the “*solvation model with state-specific polarizability*” (SMSSP) and combined it with VEM (PTES)
- Parameterised on an average of functionals (though not modern TD-DFT ones...)

Non-electrostatic terms

SMSSP

- This does away with the G_{CDS} term from SMD and replaces it with G_D which takes the form:

$$G_D = \sigma_D \alpha_M \frac{n_s^2 - 1}{n_s^2 + 2}$$

- Where σ_D is a fitted term with units of energy/volume, α_M isotropic polarisability and n_s is the refractive index of the solvent (this guy again!)
- And also with $G_{CR} = S_{CR} \gamma_S A_M$ (Cavitation-Repulsion)
 - Where S_{CR} is a unitless fitted parameter, γ_S is the air/solvent surface tension, and A_M is the SASA
- Requires manual calculation/input of of GS/ES polarisability

Non-electrostatic terms

Other models

- In 1993, Zerner and Rosch devised an explicit dispersion correction using solute and solvent calculations
- In 2010, Mennucci and Frediani devised a model that calculates G_D from refractive index and an empirical scaling factor, but doesn't use the SASA approach - Gaussian03 extension only
- In 2012, Truhlar, Cramer and co. devised SMSSP
- In 2015, Mennucci reformulated her method to correct for issues with non-polar solvents - Gaussian09 extension only
- In 2015 Truhlar, Cramer, and Marenich reinforced their methods with VEM + SMSSP + explicit solvent molecules to account for neglected h-bonding and dispersion driven centres

Non-electrostatic terms

Other models

- In 2016, Gordon and co. implemented R^{-7} terms in EFP, making them more viable for short range non-electrostatic terms (probably faster than full QM solvent)
- In 2017, Long and Isborn showed that cLR is sufficient to account for the non-electrostatic terms, if you use explicit, MD sampled solvent.
- In 2021 Floris and Amovilli devised a variational QMC method to that calculates the solvent dispersion term using the refractive index in a CASSCF framework

Excited State Non-Electrostatic Terms

My recommendation

- This needs more work... (looks like room for a PhD!)
- In the meantime, SMSSP is the best option we have, and is available in NWChem
- If you can get some of Mennucci's Gaussian modifications, I'd be interested to try them, but who on earth has Gaussian source that they want to modify...
- There seems to be a shift towards people giving up on including these terms in the model, and instead looking to explicit solvent to capture these effects. I am NOT a fan of anything that involved QMC or MD sampling, as it's just too expensive...
 - Maybe EFP might be a better option?

BONUS!! General TD-DFT Stuff

My recommendation

- Honestly, this is pretty simple:
 - Always use a range separated hybrid, or range separated double hybrid:
 - ω B97X-D, M06-2X, CAM-B3LYP and BMK are all pretty similar in behaviour, **but** BMK is a fluke and ω B97X-D uses ground state dispersion correction which aren't correct for excited states.
 - CAM-B3LYP is my go-to (FOR TD-DFT ONLY). It's reliable and numerically stable.
 - For range separated double hybrids, (SOS)- ω PBEPP86 was benchmarked as the best and for non-range separated, (SOS)-PBE-QIDH. (By Goerigk and co.)
 - Basis sets seem to not be as significant as functional or PCM errors, but diffuse functions are a must
 - With how bad the other errors are, 6-31+G(d) seems to be about as tight as we need

BONUS!! General TD-DFT Stuff

My recommendation

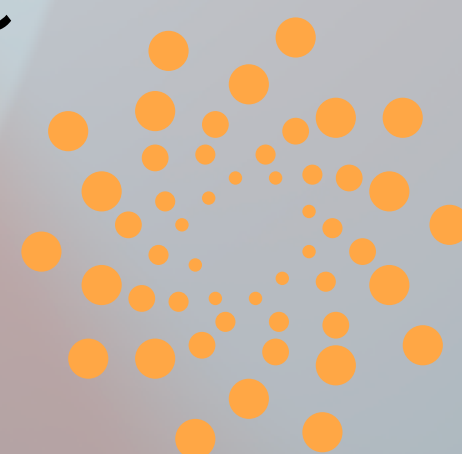
- Tamm Dancoff Approximation (TDA) is vital for triplet states, and can speed up singlet calculations, but also fails spectacularly for some species, so only use it for triplets
- While the SCF may be fine with a modest integration grid, the LR component of the TD-DFT calculation is much more sensitive and requires a tighter grid.
- The symmetry will often change/break between the GS and ES, so C_1 is good unless you're targeting a very specific state
- You never know what your QM package is doing, so if in doubt, be explicit in your settings (especially for equilibrium)

Many Thanks

- To everyone for listening, especially Sophie, Caleb and Peter for putting up with me being in pain at my desk
- To Katya (of course!)
- To Monash e-Research centre and NCI (sorry, I borrowed some of Peter's Gadi time to try and figure out how these calculations work)
- Check out our new website at mccg.erc.monash.edu :D



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