Part I: The Interaction Energy

1. Interaction energy between a charge density and an external electrostatic potential is defined.

$$U = \int \rho(\boldsymbol{R})\varphi(\boldsymbol{R})dV$$

Here, $\rho(\boldsymbol{R})$ is a charge density and $\varphi(\boldsymbol{R})$ is an electrostatic potential. Both are dependent on the coordinate $\boldsymbol{R}$.

2. The electrostatic potential can be expanded in terms of the coordinates,

$$\varphi(\boldsymbol{R}) = \varphi(0) + R_\alpha \varphi_\alpha{}'(0) + (2!)^{-1}R_\alpha R_\beta \varphi_{\alpha\beta}{}''(0) + (3!)^{-1}R_\alpha R_\beta R_\gamma \varphi_{\alpha\beta\gamma}{}''(0) + \cdots$$

The above is written in Einstein summation. So that indices written twice in each term are summed over. For example,

$$R_\alpha \varphi_\alpha{}'(0) = \sum_a^3 R_\alpha \varphi_\alpha{}'(0)$$

Term R_α is the αth coordinate and $\varphi_\alpha{}'(0)$ is the first order derivative of the electrostatic potential along the αth coordinate. Note that higher order derivatives are needed in order for a more accurate description of the electrostatic potential.

3. Then, via substitution, the interaction between a charge density and an external electrostatic potential can be written as,

$$U = \varphi(0)\int \rho(\boldsymbol{R})dV + \varphi_\alpha{}'(0)\int \rho(\boldsymbol{R})R_\alpha dV + \frac{1}{2}\varphi_{\alpha\beta}{}''(0)\int \rho(\boldsymbol{R})R_\alpha R_\beta dV + \cdots$$

This substitution allows for the calculation of the interaction energy between the charge density and the external potential to be written in separate terms. This expansion can be useful when certain assumption or conditions are considered. For example, in consider a parallel plate capacitor, the eternal electrostatic potential has a constant derivative (i.e., a homogenous electric field). The interaction energy then simply becomes,

$$U = \varphi_\alpha{}'\int \rho(\boldsymbol{R})R_\alpha dV$$

where the (0) can be removed because the electric field is the same everywhere.

4. Furthermore, the full expansion can be rewritten using terms of the electric multipole moment of the charge density,

$$U = q\varphi(0) + \mu_\alpha \varphi_\alpha'(0) + \frac{1}{2}\theta_{\alpha\beta}\varphi_{\alpha\beta}''(0) + \cdots$$

Where the q, μ_α, and $\theta_{\alpha\beta}$ are the total charge, the dipole moment, and the quadrupole moment of the charge density interacting with the external potential. A complete description of the charge density would require infinite terms if not for symmetry considerations. Note that the nth order term will be an nth order tensor. If the charge density is overall neutral, contains only an electric dipole moment, and no higher order moments due to symmetry while the external potential is only a homogenous electric field then the interaction energy can be written as,

$$U = \mu_\alpha \varphi_\beta'$$

5. Finally, due to inductive effects, each term in the multipole expansion (except the zeroth order term) is a function of the external electrostatic potential (i.e., all the derivative therein). These contributions are included via polarizabilities terms. For example, the dipole moment can be expanded as,

$$\mu_\alpha = \mu_\alpha + \alpha_{\alpha\beta}\varphi_\beta' + \frac{1}{2}\beta_{\alpha\beta\gamma}\varphi_\beta'\varphi_\gamma' + \cdots$$

where φ_β' is the first order derivative of the electrostatic potential, and the polarizability tensor $\alpha_{\alpha\beta}$ is a second order tensor containing first order derivatives of the dipole moment with respect to the electric field strength. The hyperpolarizability tensor $\beta_{\alpha\beta\gamma}$ is a third order tensor containing second order derivatives of the dipole moment with respect to the electric field strength. This expansion contains infinite terms and also includes terms such as $\beta_{\alpha,\beta\gamma}$ known as the dipole-quadrupole polarizability term which is responsible for the induced dipole due to an external electric field gradient. The higher order electric moment multipole expansion terms can also be written using such expansions.

Part II: Perturbation Theory

1. First order perturbation theory is defined as,

$$E = E_0 + \langle\psi|V_{int}|\psi\rangle$$

where E is the perturbed energy of the systems, E_0 is the unperturbed energy, ψ is the wavefunction of the state, and V_{int} is the perturbation. The energy contribution due to the

perturbation is $\langle \psi | V_{int} | \psi \rangle$.

2. The interaction between an external, homogenous electric field and a system can be written as,

$$V_{int} = -\boldsymbol{\mu} \cdot \boldsymbol{F}$$

where μ_α is the dipole moment and F_α is the electric field. This is exact if the system (1) does not have any higher order electric moments and (2) the system is not polarizable. Inserting this interaction term into the first order perturbation theory gives,

$$E = E_0 - \langle \psi | \boldsymbol{\mu} | \psi \rangle \cdot \boldsymbol{F}$$

where the electric field factor (F_α) can be taken out of the integral because the field is homogenous.

3. The transition frequency of the unperturbed system is

$$\hbar\omega = E_1 - E_0$$

where E_0 is the zero-point energy (ZPE), E_1 is the first excited state energy, $\hbar$ is Planck's constant, and ω is the transition frequency. Due to a perturbation, transition frequency can be written instead as,

$$\hbar\tilde{\omega} = [E_1 - E'_1] - [E_0 - E'_0]$$

Where the tilde indicates that the transition frequency is perturbed and the primes indicate the change in the energy level due to perturbation. Furthermore, the change in transition frequency will be the difference between the perturbed and unperturbed transition frequencies leading to the following expression,

$$\hbar\Delta\omega = \hbar\tilde{\omega} - \hbar\omega$$

Substitution causes the unperturbed energies to cancel leaving,

$$\hbar\Delta\omega = E'_1 - E'_0$$

4. In the event that the perturbation is a homogenous electric field, the following can be written,

$$E'_n = -\langle \psi_n | \boldsymbol{\mu} | \psi_n \rangle \cdot \boldsymbol{F}$$

where the integral is a diagonal element of the transition dipole matrix,

$$\boldsymbol{\mu}_{nm} = \langle \psi_n(\boldsymbol{R}) | \boldsymbol{\mu}(\boldsymbol{R}) | \psi_m(\boldsymbol{R}) \rangle_{\boldsymbol{R}}$$

This allows us to write the familiar linear Stark equation in terms of the transition dipole elements.

$$\hbar \Delta \omega = -[\boldsymbol{\mu}_{11} - \boldsymbol{\mu}_{00}] \cdot \boldsymbol{F}$$

Alternatively, the so-called "dipole difference operator" can be written,

$$\hbar \Delta \omega = -\Delta \boldsymbol{\mu}_{10} \cdot \boldsymbol{F}$$

From the simple form above, we see that if the excited state has a larger dipole moment then the ground state, then the transition frequency will go down under the influence of a homogenous electric field. This is because the electric field will stabilize the excited state more than the ground state.

5. For weaker fields, first order perturbation theory may capture most of the change in energy, but for stronger fields, higher order perturbation theory is necessary. The change in transition frequency using second order perturbation theory can be written as,

$$\hbar \Delta \omega = -\Delta \boldsymbol{\mu}_{10} \cdot \boldsymbol{F} - \frac{1}{2} \Delta \boldsymbol{\alpha}_{10} \cdot \boldsymbol{F} \cdot \boldsymbol{F}$$

where $\Delta \alpha_{10}$ is the "polarizability difference operator.

6. Following a derivation using first order time dependent perturbation theory, we can define the transition rate as,

$$\Gamma_{if} = \frac{2\pi}{\hbar} |V_{if}^2|$$

where V_{if}^2 is strength of the coupling between the initial state and the final state due to an interaction. This coupling term has the form,

$$V_{if}^2 = \left| \langle \psi_i | V_{int} | \psi_f \rangle \right|^2$$

When the interaction is an oscillating electric field, the interaction can be written as,

$$V_{int} = -\boldsymbol{\mu} \cdot \boldsymbol{F}(\omega) e^{-i\omega t}$$

then the transition rate can be written as,

$$\Gamma_{if} = \frac{2\pi}{\hbar} |F(\omega)|^2 \left| \langle \psi_i | \boldsymbol{\mu} | \psi_f \rangle \right|^2 \delta(E_f - E_i - \hbar\omega)$$

where ω is the frequency of the oscillating field. It can be seen that the transition rate Γ_{if} is proportional to the strength of the electric field $F(\omega)$ and to the couple between state ψ_i and ψ_f via the dipole moment operator $\boldsymbol{\mu}$. Furthermore, the above expression yields the selection rules via symmetry considerations of the couple states. If $\boldsymbol{\mu}(x)$ varies linearly over x then it is an odd function and therefore the integral containing states of like symmetry have forbidden transitions.

7. The peak intensity (oscillator strength) of the transition from ψ_j to ψ_i can be calculated using the following expression,

$$f_{j \to i} = \frac{2m}{3\hbar^2 e^2} E_{ij} \left| \boldsymbol{\mu}_{ij} \right|^2$$

where m is the mass of the particle and E_{ij} is the energy difference between the E_i and E_j state. The transition dipole matrix elements change due to an external homogenous electric field and can be written as,

$$\boldsymbol{\mu'}_{ij} = \boldsymbol{\mu}_{ij} + \boldsymbol{\alpha}_{ij} \cdot \boldsymbol{F} + \boldsymbol{\beta}_{ij} \cdot \boldsymbol{F} \cdot \boldsymbol{F} + \cdots$$

where $\boldsymbol{\mu'}_{ij}$ is the transition dipole moment element due to an external field, $\boldsymbol{\mu}_{ij}$ is the unperturbed transition dipole moment element, $\boldsymbol{\alpha}_{ij}$ is the transition polarizability matrix element, and $\boldsymbol{\beta}_{ij}$ is the transition hyperpolarizability matrix element. Hence, to a first order approximation, the change in peak frequency due to an external homogenous electric field is,

$$\Delta f_{j \to i} = \frac{2m}{3\hbar^2 e^2} E_{ij} \left| \boldsymbol{\alpha}_{ij} \cdot \boldsymbol{F} \right|^2$$

Part III: The Fourier Grid Hamiltonian

1. The coordinate representation of the Hamiltonian operator can be written as,

$$\langle x | \widehat{H} | x' \rangle = \langle x | \widehat{T} | x' \rangle + V(x) \delta(x - x')$$

where $\widehat{H}$ is the Hamiltonian operator, $\widehat{T}$ is the kinetic energy operator, $\widehat{V}$ is the potential energy operator, $|x\rangle$ are the eigenfunctions of the position operator $\hat{x}$. The kinetic energy operator above can be transformed by inserting the identity operator in the momentum eigenfunction basis set.

$$\langle x | \widehat{H} | x' \rangle = \frac{1}{2\pi} \int\limits_{-\infty}^{\infty} e^{ik(x-x')} T_k \, dk + V(x) \delta(x - x')$$

Where k is the momentum eigenvalue associated with the momentum eigenfunction $|k\rangle$. The integral in the kinetic energy term can be regarded as a forward, followed by an inverse, Fourier transform.

2. Replacing the continuous range of values with a discrete grid of x values allows for elements of the Hamiltonian matrix to be written as such,

$$H_{ij} = \frac{1}{\Delta x}\left\{\sum_{l=-n}^{n} \frac{e^{il2\pi(i-j)/N}}{N} T_l + V(x_i)\delta_{ij}\right\}$$

This form can be rewritten in the limit that the number of grid points reaches infinity as

$$H_{ij} = \begin{cases} \dfrac{K^2}{3} + V(x_i) & (i = j) \\ \dfrac{2K^2}{\pi^2} \dfrac{(-1)^{j-i}}{(j-i)^2} & (i \neq j) \end{cases}$$

where $K = \pi/\Delta x$

3. The above expressions consider the 1-dimensional form of the FGH method and an N-dimensional form is readily written. The basis set for the N-dimensional FGH method consists of Hartree products of position eigenfunctions of different dimensions. This can be written as,

$$\psi_i = \prod_{q=1}^{N} \left|x_k^{(q)}\right\rangle$$

The elements of the Hamilton matrix can then be written as

$$H_{ij} = \begin{cases} \dfrac{-\hbar^2}{6m}\displaystyle\prod_{q=1}^{N}\left(K^{(q)}\right)^2 + V\left(x_r^{(1)}, x_r^{(2)}, x_r^{(3)}, \dots\right) & \leftrightarrow r = s \;\forall\; x_k^{(q)} \\[2ex] \dfrac{-\hbar^2\left(K^{(s)}\right)^2}{m\pi^2}\dfrac{(-1)^{s-r}}{(s-r)^2} & \leftrightarrow \exists!\, n \in \left\{x_k^{(q)}\right\}(r \neq s) \\[2ex] 0 & \text{otherwise} \end{cases}$$

4. Finally, a complete active space self-consistent field method can also be implemented. This method involves solving the 1-dimensional Schrodinger equation in each dimension self-consistently. Following the SCF procedure, Hartree products can be built up into multi-dimensional basis functions. This Hartree product basis set is used to construct a Hamiltonian matrix which is diagonalized yielding multidimensional wavefunctions.