

Detecting the Variation of Electronic Transition Dipole Moments in Absorption Spectra

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The Condon approximation that off diagonal electronic transition dipole moments do not vary with nuclear coordinates, is not as solid an approximation in the world of ultrafast, dynamic spectroscopies as it was in the days of gas phase rovibrational spectroscopy when Condon first made the approximation. Recent scholarship shows both that such variation non-trivially effects spectroscopic observables and that many systems do indeed exhibit variation in their electronic transition dipole moments. Thus a better understanding of how such phenomenon affects even basic spectroscopic variables could be useful, as would a tool to measure the extent to which a system has a variation in its transition dipole moment. We discuss how polynomial variation with respect to the nuclear coordinate in the electronic transition dipole moment affects the interpretation of the electronic absorption spectrum and use the result to investigate the transition dipole structure of Tetracene.

I. INTRODUCTION

Edward Condon in 1928[3] made with surprisingly little justification the approximation that the electronic transition dipole did not depend on the nuclear position at all. This approximation which bears his name has always been known to be incorrect to an extent: if it the Condon approximation was always true, resonance Raman spectroscopy would not work[9].

The Condon approximation frequently pops up in electronic spectroscopy, but much recent scholarship has used nuclear variation in the transition dipole moment to explain electronic vibrational phenomenon.

There are no doubt many more we do not cite here, but among the recent work to include invoking a nontrivial transition dipole are recent work to explain graphene's anomalous Raman spectrum [5]. Furthermore, recent calculations also predict a highly noticeable transition dipole moment in photosynthetic systems[12]. There is also most probably a noticeable effect in some electron transfer systems of a varying transition dipole moment[8]. Lastly, variation in the transition dipole can cause the blurring together of effects from vibrational and electronic coherences[7].

Thus, as more and more scholarship begins to make clear the importance of variation of the transition dipole to the field of dynamic spectroscopy, it would seem to be useful to have a tool to measure these variations. While experiments can infer the presence of a nontrivial transition dipole, and it turns out a simple electronic absorption spectra will have a signature of such a variation in the electronic transition dipole moment.

II. SYSTEM SETUP

For our purposes we construct a one-mode vibrational monomer with a ground electronic state $|g\rangle$ and an excited electronic state $|e\rangle$ and assume the vibrational frequency is the same in both states. In principle, however, this method is extensible to more vibrational degrees of freedom. From this assumption, the Hamiltonian looks

like this:

$$H_0 = \sum_n \hbar\omega \left(n + \frac{1}{2}\right) |n_\gamma\rangle |g\rangle \langle g| \langle n_\gamma| \quad (\text{II.1})$$

$$+ \sum_m \left(\hbar\omega \left(m + \frac{1}{2}\right) + \omega_e \right) |m_e\rangle |e\rangle \langle e| \langle m_e| \quad (\text{II.2})$$

With the greek indices corresponding to the vibrational states and the roman indices corresponding to the electronic states. We give this system an electronic transition dipole:

$$\hat{\mu}(x) = \mu(x) (|e\rangle \langle g| + |g\rangle \langle e|) \quad (\text{II.3})$$

Where we put all the nuclear variation of the transition dipole moment into the function $\mu(x)$. Considering what a varying transition dipole may look like, we construct the simplest possible variation: a linear-varying moment, which one can transform into ladder operators for easier calculation:

$$\mu(x) = \mu_0 [1 + c (\hat{a}_\gamma + \hat{a}_\gamma^\dagger)] \quad (\text{II.4})$$

where \hat{a}_γ and \hat{a}_γ^\dagger are ladder operators in the ground state vibrational potential. One can imagine a more general form of the transition dipole for more than just linear variation:

$$\mu(x) = \mu_0 \sum_{i=0} \kappa_i x^i \quad (\text{II.5})$$

$$= \mu_0 \sum_{i=0} \epsilon_i (\hat{a} + \hat{a}^\dagger)^i \quad (\text{II.6})$$

but we will concerns ourselves exclusively with the linear variation here. Depending on the context, it can be useful to transition dipole of the transition dipole as more of a vibrational matrix element:

$$\mu_{a,b} = \langle a_\gamma | \mu(x) | b_\gamma \rangle \quad (\text{II.7})$$

which for the form specified above will look like:

$$\mu_{a,b} = \mu_0 \left[\delta_{a,b} + c \left(\sqrt{b-1} \delta_{a,b-1} + \sqrt{b} \delta_{a,b+1} \right) \right] \quad (\text{II.8})$$

III. EFFECTS ON ABSORPTION

The change in transition dipole moment from the Condon approximation will not effect the frequency of the transitions in our model, so instead we look only at peak heights: specifically the absorptivity normalized to the frequency squared

$$\frac{\epsilon(\omega)}{\omega^2} = K(\omega) = \sum_{\eta,i} h_{\eta,i} f_L(\omega, \sigma, \Delta\omega_{\eta,i}) \quad (\text{III.1})$$

where f_L is a lineshape function which integrates to unity, sigma σ is the width parameter(s) for the line-shape. Finally and most importantly, $h_{\eta,i}$ and $\Delta\omega_{\eta,i}$ are the strength and frequency, respectively, of the transition from the ground vibrational state η to the excited vibrational state i .

What one might do here is compare the k th and $k+1$ th transition strengths to ascertain the Huang Rhys Parameter S :

$$\frac{h_{\eta,k+1}}{h_{\eta,k}} = \frac{\sum_{\lambda,\nu} \mu_{\eta,\lambda}^* \mu_{\eta,\nu} O_{\lambda}^{k+1} O_{\nu}^{k+1}}{\sum_{l,n} \mu_{\eta,l}^* \mu_{\eta,n} O_l^k O_n^k} = H(\eta, k) \quad (\text{III.2})$$

Where O_{λ}^k is the Franck-Condon overlap factor between a electroic ground vibrational energy state λ and an electroic excited vibrational energy state k . If one starts out in the 0th state and assumes constant transition dipole moment(0th order as indicated in the subscript to H), the relation is quite simple:

$$H_{(0)}(0, k) = \frac{S}{k+1} \quad (\text{III.3})$$

But going one step futher to a linear-only transition dipole variation, you end up with the relation between subsequent peak heights of

$$H_{(1)}(0, k) = \frac{S}{k+1} \frac{\left| 1 + c\sqrt{S} \left(1 - \frac{k+1}{S} \right) \right|^2}{\left| 1 + c\sqrt{S} \left(1 - \frac{k}{S} \right) \right|^2} \quad (\text{III.4})$$

One of the possibly more jarring consequences of this is if you are measuring just the ratio of the $0 \rightarrow 1$ peak to the $0 \rightarrow 0$ peak then while one would expect it to just be the Huang-Rhys parameter, it would in fact be an effective Huang-Rhys parameter S_{eff}

$$S_{\text{eff}} = S \frac{\left| 1 + c\sqrt{S} \left(1 - \frac{1}{S} \right) \right|^2}{\left| 1 + c\sqrt{S} \right|^2} \quad (\text{III.5})$$

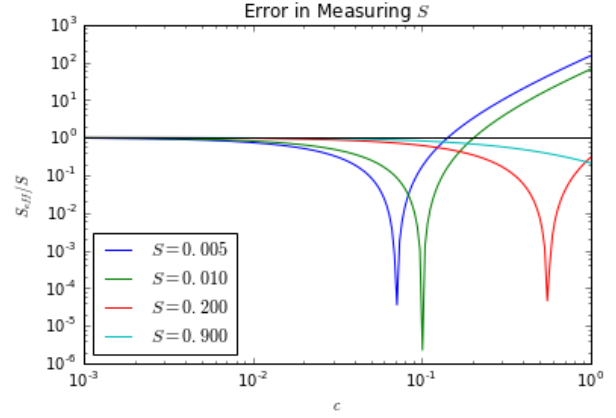


Figure 1: The measurement error S_{eff}/S as a function of S for the ratio of the $0 \rightarrow 1$ peak to the $0 \rightarrow 0$ peak, for various values of S and an entirely real linear-variation in the transition dipole moment c . This shows that the smaller the value of S , the smaller the value of c which starts causing trouble for spectroscopic analysis.

in figure 1 you can see that the smaller the value of S and the bigger the value of c , the larger the induced error in S is.

IV. CORRECTIONS TO TETRACENE

Comparing an absorption spectrum's peak heights to find the transition dipole is not new; in 1954 Fraser described how to map out the precise coordinate dependence of transition dipoles in high-resolution electronic-vibrational absorption spectra of diatomics[4]. But in solution, you have far fewer peaks so a full map is not possible. Here we describe a method to find an approximate low-order polynomial transition dipole variation for just one mode in a molecule in solution.

To demonstrate this, we take the absorption spectrum of Tetracene in dichloromethane[10] and in toluene[1]. We chose tetracene because of its important role in solar energy collection [2] and because it has a sufficiently high Huang-Rhys parameter S to have multiple line shapes showing.

We fit Equation III.1 to the addition of 5 Voigt line-shape for the Toluene spectrum and 6 Voigt lineshapes for the DCM spectrum. The Voigt profile captures more of the physics of the molecule in solution, allowing peaks to have varying amount of Gaussian and Lorentzian line-shape character, and such it fits the spectra better than simpler Gaussian and Lorentzian lineshapes in all cases. The result of this fit is shown in Figures 2 and 3. We then took the centers of the lineshapes and fit a Morse oscillator model, the results of which are summarized in Table I which allowed us to conclude that the harmonic approximation should be sufficient for this system.

Then to fit to Equation III.2, we used a Trust Region

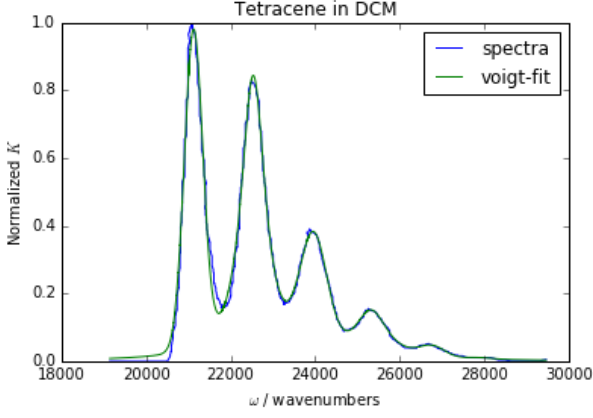


Figure 2: The fit for Voigt lineshapes to the spectra of tetracene in dichloromethane from [10]

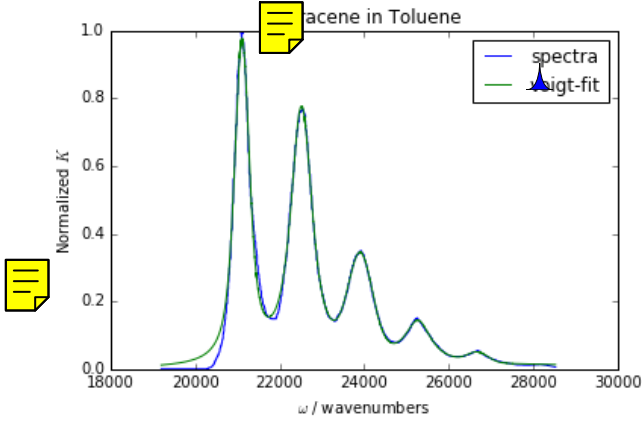


Figure 3: The fit for Voigt lineshapes to the spectra of tetracene in toluene from [1]

Reflective algorithm Least-Squares fitting procedure as implemented in Scipy[6, 11]. Because there are multiple solutions for c and θ for all orders, we include a small regularization term in the fitting procedure to keep the solutions close to the Condon value of S .

Our method was unable to find a better fit than the Condon solution for for the (1) model, but (2) gave interesting results as did (1,3). We expect odd-polynomials

Parameter	DCM	Toluene
V_0 / cm^{-1}	20421.87	20420.06
$\omega_e / \text{cm}^{-1}$	1404.74	1388.87
$\chi_e \omega_e / \text{cm}^{-1}$	-.9501	-1.5
r^2	0.9999	1.0000

Table I: Fit of the calculated peak heights to a Morse potential model. Because of the small value of $\chi_e \omega_e$ relative to ω_e , we conclude that the harmonic approximation is reasonable for this system.

Parameter	DCM	Toluene
S_{Condon}	1.52	1.185
r_{Condon}^2	.743	.829
$S_{(2)}$	1.24	1.20
$c'_{(2)}$	-0.073	0.0056
$\theta'_{(2)}/\pi$	0.0	0.0
$r_{(2)}^2$	0.794	.830
$S_{(1,3)}$	0.989	1.185
$c'_{(1)}$	-0.0168	-0.222
$\theta'_{(1)}/\pi$	0.323	1.285
$c'_{(3)}$	0.332	0.180
$\theta'_{(3)}/\pi$	0.557	1.455
$r_{(1,3)}^2$	1.000	1.000

Table II: Fit of certain parameters

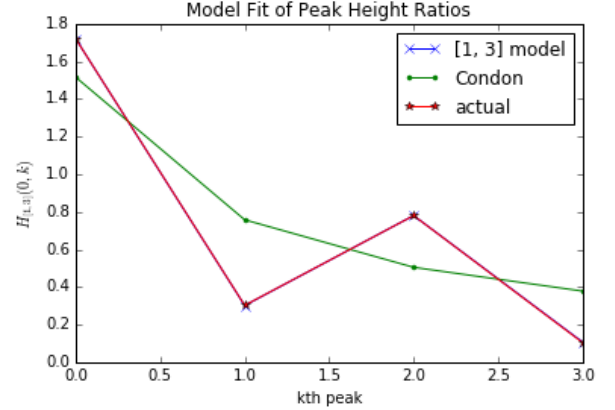


Figure 4: The Voigt-derived values of $H(0, k)$ from Tetracene in DCM, fit to the model for $H_{(1,3)}(0, k)$ and a purely Condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

to be the most physically relevant because of the broken symmetry when the molecule gets excited; we expect the molecule to preferentially absorb to the excited state when the nuclear configuration is closer to the shape of the excited state. $H_{(2)}(k, 0)$ and $H_{(1,3)}(k, 0)$ and give the results of their fitting in Table II and an example of one of these fits is in Figure 4 and 5.

We can also look at the functional form of $\mu(x)$ from transforming c' into c . The result of this for (1,3) is shown in Figure 6. Despite the slightly different values for c' and S for the (1,3) correction, the derived transition dipole moments seem roughly similar.

V. CONCLUSION

We have developed a method to provide estimates of the vibrational structure of an electronic transition dipole

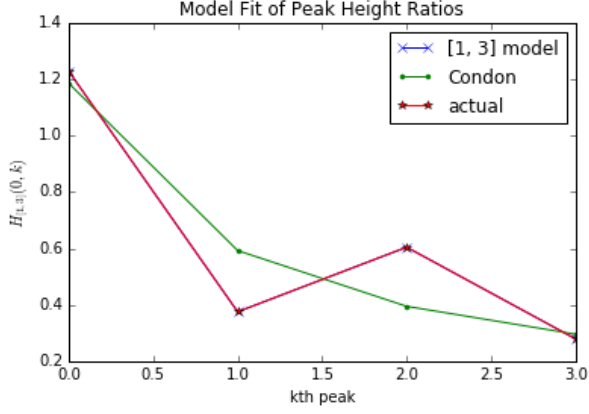


Figure 5: The Voigt-derived values of $H(0, k)$ from Tetracene in Toluene, fit to the model for $H_{(1,3)}(0, k)$ and a purely condon model. Note that the Condon model does not fit the trend very well at all whereas the non-Condon model tracks the trend very well.

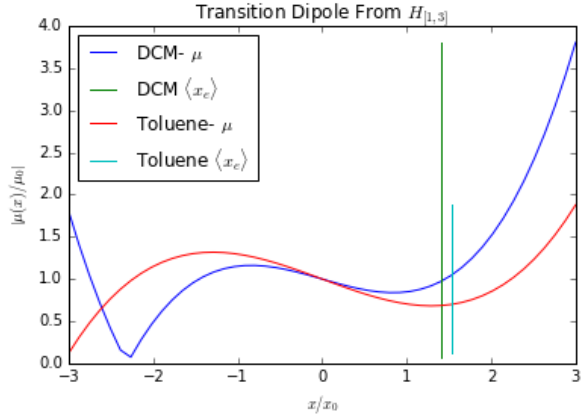


Figure 6: The fitted functional form for the transition dipole moment calculated for the Voigt-derived values of $H(0, k)$ to the model for $H_{(1,3)}(0, k)$.

moment using just an electronic absorption spectrum and applied this method to Tetracene in two different solvents.

VI. ACKNOWLEDGEMENTS

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VII. SUPPLEMENTARY INFORMATION (WILL BE REMOVED FROM PAPER, INCLUDED IN THESIS)

A. Absorption Harmonic Oscillator Model

We will find useful here the generic form of the Franck Condon Overlap factor for a displaced harmonic oscillator with the same curvature in the ground and excited states:

$$O_m^n = (-1)^n \sqrt{\frac{e^{-S} S^{m+n}}{m!n!}} \sum_{j=0}^{\min(m,n)} \frac{m!n!(-1)^j S^{-j}}{j!(m-j)!(n-j)!} \quad (\text{VII.1})$$

1. Linear Correction

To calculate the electric field ratio for a linear non-condon correction for a system starting in the 0th state:

$$\begin{aligned} \mu_{0,\lambda} &= \mu_0 \langle 0 | (1 + c_1 (\hat{a} + \hat{a}^\dagger)) | \lambda \rangle \\ &= \mu_0 (\delta_{0,\lambda} + c_1 \delta_{1,\lambda}) \end{aligned}$$

$$H_{(1)}(0, k) = \frac{\sum_{\lambda,\nu} [\delta_{0,\lambda} + c^* \delta_{\lambda,1}] [\delta_{0,\nu} + c \delta_{\nu,1}] O_\lambda^{k+1} O_\nu^{k+1}}{\sum_{l,n} [\delta_{0,l} + c^* \delta_{l,1}] [\delta_{0,n} + c \delta_{n,1}] O_l^k O_n^k} \quad (\text{VII.2})$$

$$= \frac{[O_0^{k+1} + c^* O_1^{k+1}] [O_0^{k+1} + c O_1^{k+1}]}{[O_0^k + c^* O_1^k] [O_0^k + c O_1^k]} \quad (\text{VII.3})$$

$$= \frac{|O_0^{k+1} + c O_1^{k+1}|^2}{|O_0^k + c O_1^k|^2} \quad (\text{VII.4})$$

$$= \left(\frac{O_0^{k+1}}{O_0^k} \right)^2 \frac{\left| 1 + c \frac{O_1^{k+1}}{O_0^{k+1}} \right|^2}{\left| 1 + c \frac{O_1^k}{O_0^k} \right|^2} \quad (\text{VII.5})$$

So we have several quantities to calculate:

$$O_0^{k+1} = (-1)^{k+1} \sqrt{\frac{e^{-S} S^{k+1}}{(k+1)!}} \quad (\text{VII.6})$$

$$O_1^{k+1} = (-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \sum_{j=0}^{\min(1,k+1)} \frac{(k+1)!(-1)^j S^{-j}}{j!(1-j)!(k+1-j)!} \quad (\text{VII.7})$$

$$= (-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \left[\frac{(k+1)!}{(k+1)!} - \frac{(k+1)! S^{-1}}{k!} \right] \quad (\text{VII.8})$$

$$= (-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \left[1 - \frac{(k+1)}{S} \right] \quad (\text{VII.9})$$

then the desired ratio is

$$\frac{O_1^{k+1}}{O_0^{k+1}} = \frac{(-1)^{k+1} \sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}} \left[1 - \frac{(k+1)}{S}\right]}{(-1)^{k+1} \sqrt{\frac{e^{-S} S^{k+1}}{(k+1)!}}} \quad (\text{VII.10})$$

$$= \frac{\sqrt{\frac{e^{-S} S^{1+k+1}}{(k+1)!}}}{\sqrt{\frac{e^{-S} S^{k+1}}{(k+1)!}}} \left[1 - \frac{(k+1)}{S}\right] \quad (\text{VII.11})$$

$$= \sqrt{S} \left[1 - \frac{(k+1)}{S}\right] \quad (\text{VII.12})$$

as for the other ratio:

$$O_0^k = (-1)^k \sqrt{\frac{e^{-S} S^k}{k!}} \quad (\text{VII.13})$$

$$O_1^k = (-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \sum_{j=0}^{\min(1,k)} \frac{k!(-1)^j S^{-j}}{j!(1-j)!(k-j)!} \quad (\text{VII.14})$$

first we start with the case where $k \geq 1$

$$O_1^k = (-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \left[\frac{k!}{k!} - \frac{k! S^{-1}}{(k-1)!} \right] \quad (\text{VII.15})$$

$$= (-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \left[1 - \frac{k}{S} \right] \quad (\text{VII.16})$$

if $k = 0$ then the summation above will be unity and the same equation will thus work for both. Now when we bring it back into the ratio:

$$\frac{O_1^k}{O_0^k} = \frac{(-1)^k \sqrt{\frac{e^{-S} S^{1+k}}{k!}} \left[1 - \frac{k}{S}\right]}{(-1)^k \sqrt{\frac{e^{-S} S^k}{k!}}} \quad (\text{VII.17})$$

$$= \sqrt{S} \left[1 - \frac{k}{S}\right] \quad (\text{VII.18})$$

~~we can now substitute it all in!~~

$$H_{(1)}(0, k) = \frac{S}{k+1} \frac{\left|1 + c\sqrt{S} \left(1 - \frac{k+1}{S}\right)\right|^2}{\left|1 + c\sqrt{S} \left(1 - \frac{k}{S}\right)\right|^2} \quad (\text{VII.19})$$

2. Quadratic Correction

but for a quadratic correction:

$$\begin{aligned} \mu_{0,\lambda}^{(2)} &= \mu_0 \langle 0 | \left(1 + c_2 (\hat{a} + \hat{a}^\dagger)^2\right) | \lambda \rangle \\ &= \mu_0 \langle 0 | \left(1 + c_2 (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger)\right) | \lambda \rangle \\ &= \mu_0 \left((1 + c_2) \delta_{0,\lambda} + c_2 \sqrt{2} \delta_{2,\lambda} \right) \\ &= \frac{\mu_0}{(1 + c_2)} \left(\delta_{0,\lambda} + \frac{c_2 \sqrt{2}}{(1 + c_2)} \delta_{2,\lambda} \right) \\ &= \mu'_0 (\delta_{0,\lambda} + c'_2 \delta_{2,\lambda}) \end{aligned}$$

which gives us for the peak ratios instead

$$H_{(2)}(0, k) = \frac{|O_0^{k+1} + c'_2 O_2^{k+1}|^2}{|O_0^k + c'_2 O_2^k|^2} \quad (\text{VII.20})$$

$$= \left(\frac{O_0^{k+1}}{O_0^k} \right)^2 \frac{\left|1 + c'_2 \frac{O_2^{k+1}}{O_0^{k+1}}\right|^2}{\left|1 + c'_2 \frac{O_2^k}{O_0^k}\right|^2} \quad (\text{VII.21})$$

Instead of getting algebraic expressions for $O_{n \geq 2}^k$ as we did for O_1^k , we instead implement Equation VII.1 directly in our solver.

3. 3 Correction

The cubic correction looks like so:

$$\begin{aligned} \mu_{0,\lambda}^{(3)} &= \mu_0 \langle 0 | \left(1 + c_3 (\hat{a} + \hat{a}^\dagger)^3\right) | \lambda \rangle \\ &= \mu_0 \langle 0 | \left(1 + c_3 (\hat{a} + \hat{a}^\dagger) (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger)\right) | \lambda \rangle \\ &= \mu_0 \left(\langle 0 | + c_3 \langle 1 | \left(\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger \right) \right) | \lambda \rangle \\ &= \mu_0 \left(\langle 0 | + c_3 \left(2 \langle 1 | + \sqrt{6} \langle 3 | \right) \right) | \lambda \rangle \\ &= \mu_0 \left(\delta_{0,\lambda} + c_3 \left(2 \delta_{1,\lambda} + \sqrt{6} \delta_{3,\lambda} \right) \right) \end{aligned}$$

which indicates it makes more sense to treat (1,3) and not just (3):

$$\begin{aligned} \mu_{0,\lambda}^{(1,3)} &= \mu_0 \left(\delta_{0,\lambda} + \delta_{1,\lambda} (2c_3 + c_1) + c_3 \sqrt{6} \delta_{3,\lambda} \right) \\ &= \mu_0 \left(\delta_{0,\lambda} + c'_1 \delta_{1,\lambda} + c_3 \sqrt{6} \delta_{3,\lambda} \right) \\ c'_1 &= (2c_3 + c_1) \\ c'_3 &= c_3 \sqrt{6} \\ c_1 &= \left(c'_1 - 2 \frac{c'_3}{\sqrt{6}} \right) \end{aligned}$$

4. 4 Correction

Looking at a quadratic correction:

$$\begin{aligned}
\mu_{0,\lambda}^{(4)} &= \mu_0 \langle 0 | \left(1 + c_4 (\hat{a} + \hat{a}^\dagger)^4 \right) | \lambda \rangle \\
&= \mu_0 \langle 0 | \left(1 + c_4 (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger)^2 \right) | \lambda \rangle \\
&= \mu_0 \left(\delta_{0,\lambda} + c_4 \langle 0 | (1 + \hat{a}\hat{a}) (\hat{N} + 1 + \hat{a}\hat{a} + \hat{a}^\dagger\hat{a}^\dagger) | \lambda \rangle \right) \\
&= \mu_0 \left(\delta_{0,\lambda} + c_4 \left[3\delta_{0,\lambda} + 4\sqrt{2}\delta_{2,\lambda} + 2\sqrt{6}\delta_{4,\lambda} \right] \right) \\
&= \mu_0 \left(\delta_{0,\lambda} (1 + 3c_4) + 4\sqrt{2}c_4\delta_{2,\lambda} + 2\sqrt{6}c_4\delta_{4,\lambda} \right) \\
&= \mu'_0 \left(\delta_{0,\lambda} + \frac{4\sqrt{2}c_4}{1 + 3c_4}\delta_{2,\lambda} + \frac{2\sqrt{6}c_4}{1 + 3c_4}\delta_{4,\lambda} \right)
\end{aligned}$$

much like for (3) we had to consider (1,3) to be more accurate, it makes no sense to consider (4) on its own; we'll need to introduce (2) as well to get (2,4):

$$\begin{aligned}
\mu_{0,\lambda}^{(2,4)} &= \mu_0 \left(\delta_{0,\lambda} (1 + c_2 + 3c_4) + \left(\sqrt{2}c_2 + 4\sqrt{2}c_4 \right) \delta_{2,\lambda} + 2\sqrt{6}c_4\delta_{4,\lambda} \right) H_{(\{i\})}(0, k) = \frac{S}{k+1} \frac{\left| 1 + \sum_{l=\{i\}} c'_l \frac{O_l^{k+1}}{O_0^{k+1}} \right|^2}{\left| 1 + \sum_{l=\{i\}} c'_l \frac{O_l^k}{O_0^k} \right|^2} \quad (\text{VII.22}) \\
&= \mu'_0 \left(\delta_{0,\lambda} + \frac{\sqrt{2}c_2 + 4\sqrt{2}c_4}{1 + c_2 + 3c_4}\delta_{2,\lambda} + \frac{2\sqrt{6}c_4}{1 + c_2 + 3c_4}\delta_{4,\lambda} \right) \\
c'_2 &= \frac{\sqrt{2}c_2 + 4\sqrt{2}c_4}{1 + c_2 + 3c_4} \\
c'_4 &= \frac{2\sqrt{6}c_4}{1 + c_2 + 3c_4}
\end{aligned}$$

which when inverted turns into:

$$\begin{aligned}
c_2 &= -\frac{2(\sqrt{6}c'_2 - 2\sqrt{2}c'_4)}{2\sqrt{6}c'_2 - \sqrt{2}c'_4 - 4\sqrt{3}} \\
c_4 &= \frac{c'_4(3\sqrt{2}c'_4 - 4\sqrt{3})}{(2\sqrt{6} - 3c'_4)(2\sqrt{6}c'_2 - \sqrt{2}c'_4 - 4\sqrt{3})}
\end{aligned}$$

5. Generic Correction

It becomes clear that we should be able to define an arbitrary-order correction (at least for $\eta = 0$) rather simply by adding together generic x^n operator

$$\mu_{0,\lambda} = \sum_n c_n \mu_{0,\lambda}^{(n)} = \sum_n c_n \langle 0 | (\hat{a} + \hat{a}^\dagger)^n | \lambda \rangle$$

this would then feed in to our expression for H :

where the transformation from c' back into c would have to be calculated for any individual $H_{(\{i\})}$ but is non-trivial. We saw above that the squared operator brought amplitude back to zero and in general, all even operators will bring back amplitude to all even operators in order below and the same with odd operators.

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