Here I extend the expansion of the Bloch overlap, $\langle u^n_{\boldsymbol{k}} | u^n_{\boldsymbol{k}+\delta\boldsymbol{k}} \rangle$, for general Bloch states presented in PRL 115, 166802 (2015) to third and fourth order, and note a general pattern that the only non-trivial terms are of first and second order, but that there is an additional second order term, $-\mathcal{A}_i\mathcal{A}_j dk_i dk_j/2$, not obtained in the PRL paper.

A Physical Motivation

In principle, in a gapped semiconductor the low energy excitons (with large Bohr radius) will have the full symmetries of the vacuum and will consequently exhibit a hydrogenic/Rydberg spectrum of energy states. However the low energy excitons in the TMDs MoS_2 and WS_2 exhibit strongly non-hydrogenic energy spectra.

The eigenvalue problem for the exciton energy levels E_ν is:

$$(\Delta_{\boldsymbol{k}} - E_\nu)A_\nu(\boldsymbol{k}) - \frac{1}{S}\sum_{\boldsymbol{k}'} \frac{2\pi e^2}{\epsilon|\boldsymbol{k}-\boldsymbol{k}'|} \langle u^c_{\boldsymbol{k}} | u^c_{\boldsymbol{k}'} \rangle \langle u^v_{\boldsymbol{k}'} | u^v_{\boldsymbol{k}} \rangle A_\nu(\boldsymbol{k}') = 0 \tag{1}$$

where $\Delta_{\boldsymbol{k}}$ is the energy gap, E_ν is the orbital energy level of the orbital ν, A_ν is the amplitude of the orbital ν, S is the system quantization area, e is the electron charge, ϵ is the (screened) dielectric constant, and $|u^n_{\boldsymbol{k}}\rangle$ are the Bloch wavefunctions.

The two terms contributing to non-hydrogenic spectra are the dielectric constant and the Bloch overlaps $\langle u^n_{\boldsymbol{k}} | u^n_{\boldsymbol{k}'} \rangle$. Here, we consider the Bloch overlaps.

The Expansion

In Eqn. 1, the largest contributions come when $\boldsymbol{k}' \sim \boldsymbol{k}$, so we are interested in overlaps of the form:

$$s^n_{\boldsymbol{k},\boldsymbol{k}+\delta\boldsymbol{k}} := \langle u^n_{\boldsymbol{k}} | u^n_{\boldsymbol{k}+\delta\boldsymbol{k}} \rangle \tag{2}$$

Naïvely, we can Taylor expand this to find:

$$s^n_{\boldsymbol{k},\boldsymbol{k}+\delta\boldsymbol{k}} = 1 + \langle u^n_{\boldsymbol{k}} | \partial_i | u^n_{\boldsymbol{k}} \rangle d_i + \tfrac{1}{2}\langle u^n_{\boldsymbol{k}} | \partial_{ij} | u^n_{\boldsymbol{k}} \rangle d_{ij} + \dots \tag{3}$$

where we use Einstein summation notation for repeated indices, and $\partial_i = \partial/\partial k_i$, $d_i = dk_i$.

However, this overlap is not gauge invariant under the $U(1)$ gauge transformation:

$$|u^n_{\boldsymbol{k}}\rangle \mapsto e^{i\alpha(\boldsymbol{k})}|u^n_{\boldsymbol{k}}\rangle \tag{4}$$

since the partial derivatives pull down $\alpha(\boldsymbol{k})$ terms that do not cancel.

What *is* gauge invariant is the overlap over a loop:

$$s^n_{\boldsymbol{k},\circ} := \prod_{\boldsymbol{k}_i \in \circ} \langle u^n_{\boldsymbol{k}_i} | u^n_{\boldsymbol{k}_i+\delta\boldsymbol{k}_i} \rangle$$

It will be easier to work with a sum than a product, so we take the exponential of a logarithm:

$$\begin{aligned} s^n_{\boldsymbol{k},\circ} &= e^{\ln(s^n_{\boldsymbol{k},\circ})} \\ &= e^{\sum_{\boldsymbol{k}_i\in\circ} \ln(\langle u^n_{\boldsymbol{k}_i} | u^n_{\boldsymbol{k}_i+\delta\boldsymbol{k}_i} \rangle)} \end{aligned} \tag{5}$$

We now consider the logarithm of the overlaps, which we express as in Eq. 3, letting $|u\rangle := |u^n_{\boldsymbol{k}}\rangle$:

$$\begin{aligned}\ln(\langle u^n_{\boldsymbol{k}_i}|u^n_{\boldsymbol{k}_i+\delta\boldsymbol{k}_i}\rangle) &= \ln(1+\langle u|\partial_i|u\rangle d_i + \tfrac{1}{2}\langle u|\partial_{ij}|u\rangle d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} + \dots) \\ &= \langle u|\partial_i|u\rangle d_i + \tfrac{1}{2}\langle u|\partial_{ij}|u\rangle d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} \\ &\quad - \tfrac{1}{2}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle d_{ij} - \tfrac{1}{2}\langle u|\partial_i|u\rangle\langle u|\partial_{jk}|u\rangle d_{ijk} \\ &\quad + \tfrac{1}{3}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_k|u\rangle d_{ijk} + \dots\end{aligned} \tag{6}$$

Where we used the expansion:

$$\ln(1+x) = x - \tfrac{1}{2}x^2 + \tfrac{1}{3}x^3 - \dots \tag{7}$$

and abused notation (the indices in different terms are different).

Now, we identify the Berry connection and the Fubini-Study metric:

$$i\mathcal{A}_i = \langle u|\partial_i|u\rangle \tag{8}$$

$$g_{ij} = \langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle - \langle u|\partial_{ij}|u\rangle \tag{9}$$

So we see that:

$$\begin{aligned}\ln(\langle u^n_{\boldsymbol{k}_i}|u^n_{\boldsymbol{k}_i+\delta\boldsymbol{k}_i}\rangle) &= i\mathcal{A}_i d_i - \tfrac{1}{2}g_{ij}d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} \\ &\quad + \tfrac{1}{2}\langle u|\partial_i|u\rangle(\langle u|\partial_j|u\rangle\langle u|\partial_k|u\rangle - \langle u|\partial_{jk}|u\rangle)d_{ijk} \\ &\quad - \tfrac{1}{6}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_k|u\rangle d_{ijk} + \dots\end{aligned} \tag{10}$$

or:

$$\ln(\langle u^n_{\boldsymbol{k}_i}|u^n_{\boldsymbol{k}_i+\delta\boldsymbol{k}_i}\rangle) = i\mathcal{A}_i d_i - \tfrac{1}{2}g_{ij}d_{ij} + \tfrac{1}{2}i\mathcal{A}_i g_{jk}d_{ijk} + \tfrac{1}{6}i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} + \dots \tag{11}$$

Now, if we make the loop infinitesimal, then:

$$\begin{aligned}s^n_{\boldsymbol{k},\cdot} &= 1 + i\mathcal{A}_i d_i - \tfrac{1}{2}g_{ij}d_{ij} + \tfrac{1}{2}i\mathcal{A}_i g_{jk}d_{ijk} + \tfrac{1}{6}i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} \\ &\quad + \tfrac{1}{2}(-\mathcal{A}_i\mathcal{A}_j d_{ij} - i\mathcal{A}_i g_{jk}d_{ijk}) - \tfrac{1}{6}i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} + \dots\end{aligned} \tag{12}$$

$$= \boxed{1 + i\mathcal{A}_i d_i - \tfrac{1}{2}(g_{ij} + \mathcal{A}_i\mathcal{A}_j)d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} + \dots} \tag{13}$$

where as usual:

$$e^x = 1 + x + \tfrac{1}{2}x^2 + \tfrac{1}{6}x^3 + \dots \tag{14}$$

This overlap can then be expressed in terms of the Berry curvature instead of the Berry connection by way of Stoke's theorem:

$$i\mathcal{A}_i d_i \mapsto i\boldsymbol{\Omega}\cdot d\boldsymbol{S}_k$$

Now, to fourth order we have:

$$\begin{aligned}\ln(\langle u^n_{\boldsymbol{k}_i}|u^n_{\boldsymbol{k}_i+\delta\boldsymbol{k}_i}\rangle) &= \ln(1+\langle u|\partial_i|u\rangle d_i + \tfrac{1}{2}\langle u|\partial_{ij}|u\rangle d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} + \tfrac{1}{24}\langle u|\partial_{ijkl}|u\rangle + \dots) \\
&= \langle u|\partial_i|u\rangle d_i + \tfrac{1}{2}\langle u|\partial_{ij}|u\rangle d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} + \tfrac{1}{24}\langle u|\partial_{ijkl}|u\rangle d_{ijkl} \\
&\quad - \tfrac{1}{2}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle d_{ij} - \tfrac{1}{2}\langle u|\partial_i|u\rangle\langle u|\partial_{jk}|u\rangle d_{ijk} - \tfrac{1}{6}\langle u|\partial_i|u\rangle\langle u|\partial_{jkl}|u\rangle d_{ijkl} \\
&\quad - \tfrac{1}{8}\langle u|\partial_{ij}|u\rangle\langle u|\partial_{kl}|u\rangle d_{ijkl} + \tfrac{1}{2}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_{kl}|u\rangle d_{ijkl} \\
&\quad + \tfrac{1}{3}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_k|u\rangle d_{ijk} - \tfrac{1}{4}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_k|u\rangle\langle u|\partial_l|u\rangle d_{ijkl} + \dots \\
&= i\mathcal{A}_i d_i - \tfrac{1}{2}g_{ij}d_{ij} + \tfrac{1}{2}i\mathcal{A}_i g_{jk}d_{ijk} + \tfrac{1}{6}i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} \\
&\quad - \tfrac{1}{6}i\mathcal{A}_i\langle u|\partial_{jkl}|u\rangle d_{ijkl} + \tfrac{1}{24}\langle u|\partial_{ijkl}|u\rangle d_{ijkl} \\
&\quad - \tfrac{1}{8}\langle u|\partial_{ij}|u\rangle\langle u|\partial_{kl}|u\rangle d_{ijkl} + \tfrac{1}{2}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_{kl}|u\rangle d_{ijkl} \\
&\quad - \tfrac{1}{4}\langle u|\partial_i|u\rangle\langle u|\partial_j|u\rangle\langle u|\partial_k|u\rangle\langle u|\partial_l|u\rangle d_{ijkl} + \dots \\
&= i\mathcal{A}_i d_i - \tfrac{1}{2}g_{ij}d_{ij} + \tfrac{1}{2}i\mathcal{A}_i g_{jk}d_{ijk} + \tfrac{1}{6}i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} \\
&\quad - \tfrac{1}{8}g_{ij}g_{kl}d_{ijkl} + \tfrac{1}{4}\mathcal{A}_i\mathcal{A}_j g_{kl}d_{ijkl} + \tfrac{1}{8}\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k\mathcal{A}_l d_{ijkl} \\
&\quad + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} - \tfrac{1}{6}i\mathcal{A}_i\langle u|\partial_{jkl}|u\rangle d_{ijkl} + \tfrac{1}{24}\langle u|\partial_{ijkl}|u\rangle d_{ijkl} + \dots\end{aligned} \tag{15}$$

$$\begin{aligned}s^n_{\boldsymbol{k},\cdot} &= 1 + i\mathcal{A}_i d_i - \tfrac{1}{2}g_{ij}d_{ij} + \tfrac{1}{2}i\mathcal{A}_i g_{jk}d_{ijk} + \tfrac{1}{6}i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} \\
&\quad - \tfrac{1}{8}g_{ij}g_{kl}d_{ijkl} + \tfrac{1}{4}\mathcal{A}_i\mathcal{A}_j g_{kl}d_{ijkl} + \tfrac{1}{8}\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k\mathcal{A}_l d_{ijkl} \\
&\quad + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} - \tfrac{1}{6}i\mathcal{A}_i\langle u|\partial_{jkl}|u\rangle d_{ijkl} + \tfrac{1}{24}\langle u|\partial_{ijkl}|u\rangle d_{ijkl} \\
&\quad + \tfrac{1}{2}[-\mathcal{A}_i\mathcal{A}_j d_{ij} - i\mathcal{A}_i g_{jk}d_{ijk} + \tfrac{1}{4}g_{ij}g_{kl}d_{ijkl} - \mathcal{A}_i\mathcal{A}_j g_{kl}d_{ijkl} - \tfrac{1}{3}\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k\mathcal{A}_l d_{ijkl} + \tfrac{1}{3}i\mathcal{A}_i\langle u|\partial_{jkl}|u\rangle d_{ijkl}] \\
&\quad + \tfrac{1}{6}[-i\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k d_{ijk} + \tfrac{3}{2}\mathcal{A}_i\mathcal{A}_j g_{kl}d_{ijkl}] \\
&\quad + \tfrac{1}{24}\mathcal{A}_i\mathcal{A}_j\mathcal{A}_k\mathcal{A}_l d_{ijkl} + \dots \\
&= \boxed{1 + i\mathcal{A}_i d_i - \tfrac{1}{2}(g_{ij} + \mathcal{A}_i\mathcal{A}_j)d_{ij} + \tfrac{1}{6}\langle u|\partial_{ijk}|u\rangle d_{ijk} + \tfrac{1}{24}\langle u|\partial_{ijkl}|u\rangle d_{ijkl} + \dots}\end{aligned} \tag{16}$$

So we see that the only higher order terms with order above two are those of the naïve Taylor series. In fact, this generalizes to arbitrary order because the exponential of the logarithm is just the identity, and we are only decomposing into (geometric) expressions of first and second order.

Some thoughts:

- Can you construct a model such that the higher order derivatives vanish, i.e. $\langle u|\partial_{ijk}|u\rangle = 0$? Since we are in 2D, this means $|u\rangle$ is at most linear in k_x and k_y, i.e. $|u\rangle = c_0 + c_x k_x + c_y k_y + c_{xy}k_x k_y$, but this is only periodic for a uniform band $|u\rangle = c_0$ where $c_x = c_y = c_{xy} = 0$.
- Can this be extended to off diagonal terms $\langle u^n_{\boldsymbol{k}}|u^m_{\boldsymbol{k}+\delta\boldsymbol{k}}\rangle$?