Thomas-Reiche-Kuhn sum rules

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The Thomas-Reiche-Kuhn sum rule represents one of the most elegant and fundamental results in quantum mechanics, connecting classical and quantum descriptions of atomic oscillators. This sum rule states that the total oscillator strength for all possible transitions from a given atomic state equals the number of electrons in the atom.

blog: https://tetraquark.vercel.app/posts/Thomas_Reiche_Kuhn_sum_rules/?src=pdf

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In perturbation theory, one frequently encounters the following summation:

$$S \equiv \sum_m (E_m - E_n)|\langle m|X|n\rangle|^2 \tag{1}$$

where $|m\rangle$ and $|n\rangle$ are eigenstates of $H = P^2/2m + V(X)$, and we want to prove that the summation is equal to $\frac{\hbar^2}{2m}$.

We first convert $E_m - E_n$ term into a commutation as follows.

$$(E_m - E_n)\langle m|X|n\rangle = \langle m|[H, X]|n\rangle = \langle m|[\frac{P^2}{2\mu}, X]|n\rangle = \frac{-i}{\mu}\langle m|P|n\rangle \tag{2}$$

So we have,

$$\begin{aligned} S &= \frac{-i}{\mu}\sum_m \langle m|P|n\rangle\langle n|X|m\rangle = \frac{-i}{m}\langle n|X|\sum_m |m\rangle\langle m|P|n\rangle \\ &= \frac{-i\hbar}{m}\langle n|XP|n\rangle \end{aligned} \tag{3}$$

Note that S is manifestly real from its definition, so we can add up its complex conjugate which will simply double it.

$$\begin{aligned} S &= \frac{S + S^*}{2} = \frac{-i\hbar}{2m}\langle n|XP|n\rangle + \frac{i\hbar}{2m}\langle n|PX|n\rangle \\ &= \frac{\hbar^2}{2m}\langle n|[X, P]|n\rangle = \frac{1}{2m} \end{aligned} \tag{4}$$

Let's test the sum rule on the nth state of the oscillator. For the harmonic oscillator,

$$\begin{aligned} S &= w\sum_m (m+1/2-n-1/2)|\langle m|X|n\rangle|^2 \\ &= w\sum_m (m-n)\frac{\hbar^2}{2mw}\left(\sqrt{n+1}\delta_{m,n+1}+\sqrt{n}\delta_{m,n-1}\right)^2 \\ &= \frac{\hbar^2}{2m}(n+1-n) = \frac{\hbar^2}{2m}, \end{aligned} \tag{5}$$

which agrees with the sum rule.