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Kvantmehaanika ja spektroskoopia

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3. How is looks like the equation for first order approximation of perturbation theory (degenerate case)? Derive.

For a degenerate energy level E_n^0 with eigenstates $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr}$, the zeroth-order wavefunction is an arbitrary linear combination:

$$\psi_n^0 = \sum_{i=1}^{r} c_i \psi_{ni}.$$

Under perturbation $\hat{H} = \hat{H}_0 + \hat{H}'$, the first-order correction satisfies:

$$\boxed{(\hat{H}_0 - E_n^0)\psi_n^1 = (E_n^1 - \hat{H}')\psi_n^0.}$$

How was this equation obtained?

where ψ_n^1 and E_n^1 are the first order improvements to the wave equation and energy eigenvalues. Since we operate in the subspace, corresponding to E_n^0, we take zeroth order wave function ψ_n^0 as an arbitrary linear combination of functions $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr}$. Analysing the equation

$$(\hat{H}_0 - E_n^0)\psi_n^1 = \sum_{j=1}^{r} c_j (E_n^1 - \hat{H}')\psi_{nj}.$$

Multiplying from left to ψ_{ni}^*, we integrate and use $\int \psi_{ni}^* \psi_{nj}\, dV = \delta_{ij}$.

Left side of the previous equality is equal to zero,

$$\int \psi_{ni}^* (\hat{H}_0 - E_n^0)\psi_n^1\, dV = 0.$$

The right side is also equal to zero

$$\sum_{j=1}^{r} c_j \int \psi_{ni}^* (E_n^1 - \hat{H}')\psi_{nj}\, dV = 0.$$

Introducing matrix elements

$$H'_{ij} = \int \psi_{ni}^* \hat{H}' \psi_{nj}\, dV$$

and taking into account the orthonormality of $\psi_{n1}, \psi_{n2}, \ldots, \psi_{nr}$, we get he following equations

$$\sum_{j=1}^{r} (E_n^1 \delta_{ji} - H'_{ij}) c_j = 0, \quad i = 1, 2, \ldots, r.$$

Approximations to energy. There are nontrivial solutions, if the determinant is equal to zero. Denoting $\varepsilon = E_n^1$, we have

$$\begin{vmatrix} \varepsilon - H'_{11} & -H'_{12} & \dots & -H'_{1r} \\ -H'_{21} & \varepsilon - H'_{22} & \dots & -H'_{2r} \\ \vdots & \vdots & \ddots & \vdots \\ -H'_{r1} & -H'_{r2} & \dots & \varepsilon - H'_{rr} \end{vmatrix} = 0.$$

From it we have some r-th order equation for

$$\varepsilon^r + \alpha_1 \varepsilon^{r-1} + \dots + \alpha_r = 0,$$

which has r real valued solutions (roots)

$$\varepsilon_1, \varepsilon_2, \dots, \varepsilon_r$$

Therefore, all nonzero solutions ε_i give us new energy levels

$$E_n^i = E_n^0 + \varepsilon_i.$$

For each ε_i one can solve the system and find the corresponding $c_1^i, c_2^i, \dots, c_r^i$, which in turn gives the wave function

$$\psi_n^i = \sum_{j=1}^{r} c_j^i \psi_{nj}.$$

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8. Equation for the time dependent expansion coefficients $C_m(t)$ of the total wave function. Representation of the solution of this equation in the form of expansion into a series of perturbation theory approximations. The relationship for these coefficients and the probability of an interlevel transition.

The time-dependent Schrödinger equation for a system under a perturbation $H'(t)$ is:

$$i\hbar\frac{\partial\Psi}{\partial t} = (\hat{H}_0 + \hat{H}'(t))\Psi(\vec{r}).$$

where $\hat{H}_0$ is the unperturbed Hamiltonian. The wave function is expanded as:

This is the wave function for which eigenvalue problem?

$$\Psi(\vec{r},t) = \sum_n C_n(t)e^{-iE_nt/\hbar}\boxed{\psi_n.}$$

Substituting this into the Schrödinger equation gives the equation for $C_m(t)$:

$$i\hbar\frac{dC_m(t)}{dt} = \sum_n e^{i\omega_{mn}t}H'_{mn}C_n(t), \quad m = 1, 2, \ldots$$

where $\omega_{mn} = (E_m - E_n)/\hbar$ and $H'_{mn}(t) = \langle\psi_m|H'(t)|\psi_n\rangle$.
The coefficients $C_m(t)$ are expanded as:

????

$$C_m(t) = C_m^{(0)}(t) + \boxed{C_m^{(1)}}(t) + C_m^{(2)}(t) + \cdots.$$

The zeroth-order solution is $\boxed{C_m^0 = \delta_{mn}.}$ The first-order correction is:

$$C_m^1 = \frac{1}{i\hbar}\int_0^t e^{i\omega_{mn}\tau}H'_{mn}d\tau.$$

For a harmonic perturbation $\hat{H}'(t) = \hat{h}e^{-i\omega t} + \hat{h}^+e^{i\omega t}$:

$$C_m^1 = -\frac{1}{\hbar}\left(h_{mn}\frac{e^{i(\omega_{mn}-\omega)t} - 1}{\omega_{mn} - \omega} + h_{mn}^+\frac{e^{i(\omega_{mn}+\omega)t} - 1}{\omega_{mn} + \omega}\right).$$

The transition probability is:

$$\boxed{P_{nm}(t) = |C_m(t)|^2.}$$

This is an unsubstantiated claim.

For long times, the transition rate becomes:

$$\frac{dP_{nm}}{dt} = \frac{2\pi|h_{mn}|^2t}{\hbar^2}\delta(\omega_{mn} - \omega).$$

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13. What is the meaning of the theorem on the relationship between spin and statistics? 33

The spin-statistics theorem is a theory that establishes a connection between the intrinsic spin of particles and their quantum statistics. It states:

Particles with integer spin (0, 1, 2, ...) obey Bose-Einstein statistics and are called bosons. Their wavefunctions are symmetric under particle exchange, and they can occupy the same quantum state.

$$f(E,T) = \frac{1}{e^{E/kT} - 1}.$$

Particles with half-integer spin (1/2, 3/2, ...) obey Fermi-Dirac statistics and are called fermions. Their wavefunctions are antisymmetric under particle exchange, and they follow the Pauli exclusion principle, meaning no two fermions can occupy the same quantum state.

$$f(E,T) = \frac{1}{e^{(E-\mu)/kT} + 1}.$$

μ - chemical potential