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Kvantmehaanika ja spektroskoopia

Loengud 14-16

3. What does the equation for first order approximation of perturbation theory (degenerate case) look like? Derive.

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We start with already solved eigenvalue problem $\widehat{H}_0\Psi_n^0 = E_n^0\Psi_n^0$ so that means we already know the energies and corresponding eigenfunctions, and continue on the assumption that for each energy there is only one eigenfunction.

Now we have to solve eigenvalue problem $\widehat{H}\Psi_n = E_n\Psi_n$ where $\widehat{H} = \widehat{H} + \widehat{H}'$. The additional term $\widehat{H}'$ is the small perturbation, its energy being small compared to E_n and the difference between levels. Then we will write the energy operator as $\widehat{H} = \widehat{H} + \lambda\widehat{H}'$ where λ is some parameter which will help us to compare terms of similar order of value.

Form series expansion is as follows:

$E_n = E_n^0 + \lambda E_n^1 + \lambda E_n^2 + ...$

"We will get", but how? The process of getting is the most interesting.

$\Psi_n = \Psi_n^0 + \lambda\Psi_n^1 + \lambda\Psi_n^2 + ...$

From these we will get the first approximation from

$\widehat{H}_0\Psi_n' + \widehat{H}'\Psi_n^0 = E_n^0\Psi_n^1 + E_n'\Psi_n^0$ or $\left(\widehat{H}_0 - E_n\right)\Psi_n^1 = \left(E_n^1 - \widehat{H}'\right)\Psi_n^0$.

From here we find the approximations to energy and wave functions. The first order of wave function can be expressed as a serie $\Psi_n^1 = \sum_m a_m^1\Psi_m^0$ where Ψ_n^0 is a complete orthonormal system of functions. Substituting this to the equation and using the fact that Ψ_n^0 are the eigenfunctions of $\widehat{H}_0$ we get $\sum_m a_m^1\left(E_m^0 - E_n^0\right)\Psi_m^0 = \left(E_n^1 - \widehat{H}'\right)\Psi_n^0$.

This is a new wavefunction and energy?

Multiplying from the left with the Ψ_k^0 conjugated and integrating we get

$a_k^1\left(E_k^0 - E_n^0\right) = E_n^1\delta_{kn} - H_{kn}'$ where $H_{kn}' = \int\left(\Psi_k^0\right) * \widehat{H}'\Psi_n^0 dV$ are the elements of the matrix of the perturbation operator.

If $k = n$ we will obtain the first order correction to energy $E_n^1 = H_{nn}'$ -the diagonal elements of the perturbation operator.

If $k \neq n$ we obtain the coefficients to the first approximation of the wave function $a_k^1 = \frac{H_{kn}'}{E_n^0 - E_k^0}$.

One of the coefficients – a_n^1 – will be determined from the normalization of the first order wave function $\int\left(\Psi_n^0 + \lambda\sum_m a_m^1\Psi_m^0\right)*\left(\Psi_n^0 + \lambda\sum_m a_m^1\Psi_m^0\right)dV = 1$, so in the first order approximation of λ coefficient a_n^1 must satisfy $a_n^1 + \left(a_n^1\right)* = 0$. As it is imaginary, we can substitute it as $a_n^1 = 0$.
So in conclusion the first order approximation $(\lambda = 1)$ is

$$E_n = E_n^0 + H_{nn}'$$

$$\Psi_n = \Psi_n^0 + \sum_{k\neq n}\frac{H_{nn}'}{E_n^0 - E_k^0}\Psi_k^0$$

10. Which formula can be used to evaluate the number of photons radiated by an atom per one second (for transition n -> m)? Derive and explain. 5

To evaluate the number of photons radiated by an atom in one second when an atom transitions from energy level n to m we can use Einstein's coefficient $A_{nm} = \frac{2\pi\hbar\omega^3}{c^2}B_{mn}$ which shows the relation between spontaneous and induced transitions.
From his radiation theory we get that for induced radiation the probabilities are connected as follows: $\frac{dP_{mn}}{dt} = B_{mn}\rho(\omega) = B_{nm}\rho(\omega) = \frac{dP_{nm}}{dt}$ where $\rho(\omega)$ is the intensity of external radiation and $B_{mn} = B_{nm}$ is the probability of inner transitions.

The same result can be derived in quantum mechanics $\frac{dP_{mn}}{dt} = \frac{\pi e^2 E_0^2}{\hbar^2}\left|z_{mn}\right|^2 = \frac{dP_{nm}}{dt}$ where $z_{mn} =< \Psi_m|z|\Psi_n >= \int \Psi_m * z\, \Psi_n dV$ and $\left|z_{mn}\right|^2 = \left|z_{nm}\right|^2$. As E_0^2 characterizes the intensity of the external radiation we can say that the probability of atomic transitions $B_{mn} = B_{nm} \approx \left|z_{mn}\right|^2$.
That in turn shows that when using Einstein's coefficient we can analyze the number of photons radiated by an atom by only calculating the matrix elements of coordinates.

13. What is the meaning of the theorem on the relationship between spin and statistics? 10

The spin-statistics theorem relates a particle's intrinsic spin to the statistics that the particle obeys. All particles that can move in 3 dimensions have either integer or half-integer spin. This theorem divides all particles into two classes - bosons and fermions.
Overall this theorem describes what kind of particles can exist in our universe and how they behave when piled up.
Bosons (Bose particles) have an integer spin 0,1,2,... . In each quantum state there can be an infinitely large number of bosons. All particles in the same state also have the same wave function, and the probability of finding one can be calculated using Bose-Einstein distribution function. Bosons are for example photons and gluons. Aga kus on valemid?

Fermions (Fermi particles) on the other hand, have a half-integer spin value 1/2, 3/2, 5/2, … . Only one fermion can be located in a given quantum state, according to the Pauli exclusion principle. The probability of finding one such particle can be calculated using the Fermi-Dirac distribution function. Fermions are for example electrons and neutrons.