

Perturbation Theory and Dalgarno-Lewis (DL) Method in Presence of Multiple Laser Beams

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Abstract

The evaluation of second and higher order perturbation of energy by iterative solution of Schrodinger's equation, rather than evaluation of matrix element is described.

Key words: perturbed hamiltonian, dalgarno operator

Introduction

While there are many ways to solve Schrodinger equation (SE) analytically, we cannot always obtain an exact solution. Therefore, we must move on to different approaches to obtain more precise results. For example, if the potential energies are known then we can formulate their corresponding Hamiltonians to solve Schrodinger equations very precisely. Hence no such approximations are required for the preceding case. While there are many such Hamiltonians which can be solve fairly easily, there are many more whose solutions can only be approximated numerically. We therefore have to use the widely accepted Perturbation Theory to find approximate solutions of such Hamiltonians—provided that they are similar to the ones which are fairly easy to solve.

Perturbation theory works best when the system's total energy is "perturbed" by a small additional potential energy (Messsiah 1962). The total Hamiltonian can be expressed as a sum of an unperturbed Hamiltonian

(\hat{H}_0) and a perturbed Hamiltonian (\hat{H}'),

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

The plan is to expand the system of Hamiltonian, and hence the total energy, into a sum of terms involving higher and higher powers of \hat{H}' , similar to a Taylor series expansion of a function around some value. Since the perturbation is small, we only have to keep

the first few terms (typically two or three terms) to obtain a close approximation to the actual total energy.

We must be careful when using the perturbation theory because the perturbing potential should not change the number of bound states of the considered atoms in the system. We can also assume that the unperturbed states of the atoms in consideration form a complete set. We can then express the corrected states as linear combinations of the unperturbed states.

However, if the perturbing potential changes the Hamiltonian of the system such that the number of bound states is increased by one, this new state must have come from the unbounded region. This is a problem because the unbounded region contains a continuum of energies. So while perturbation theory is a very useful tool, it is not *always* the method of choice.

The time independent (TI) form of the theory is best suited to the problems with discrete energy spectrum. The time dependent (TD) form is useful for problems where there is a continuum of energy states; and here, the product $H't / \hbar$ must less than unity. In both the forms, the solution is obtained by expanding Eigenvalues and Eigen-functions in a series of small parameters that represents the strength of perturbing terms. The TISE

$$\hat{H}\Psi = E\Psi$$

and for TDSE,

$$\hat{H}\Psi(r,t) = i\hbar \frac{\partial \Psi(r,t)}{\partial t}$$

The solution of TDSE as,

$$\Psi(r,t) = \sum_n C_n(t) \psi_n(r) e^{-iE_n t/\hbar}$$

Here $C_n(t)$ is the expansion coefficient which is our more interest.

From TDSE, and using initial state as ground state

$$(\hat{H}_0 \psi_n = E_n \psi_n)$$

Hence, writing in Dirac Notation

$$i\hbar \sum_n \frac{\partial C_n(t)}{\partial t} e^{-iE_n t/\hbar} |\psi_n(r)\rangle = \sum_n C_n(t) e^{-iE_n t/\hbar} H^1 |\psi_n(r)\rangle$$

Multiplying by bra vector $\langle \psi_m |$ in both sides and integrating over all the space

$$i\hbar \dot{C}_m(t) = \sum_n C_n(t) e^{-i(E_n - E_m)t/\hbar} H^1_{mn}$$

$$= \sum_n C_n(t) e^{-i\omega_{nm}t} H^1_{mn} \dots \dots \dots (1)$$

Where, $\hbar\omega_{nm} = E_n - E_m$

$\hbar\omega_{nm}$ is known as transition energy.

Assuming the system is in Eigen-state $|\psi_n\rangle$ at $t=0$, we can express the expansion coefficient for the first order perturbation as

$$i\hbar \dot{C}_m^{(1)}(t) = C_n^{(0)} e^{-i\omega_{nm}t} H^1_{mn}, m \neq n$$

$$C_m^{(1)}(t) = (i\hbar)^{-1} \int dt e^{-i\omega_{nm}t} H^1_{mn}(t) \dots \dots \dots (2)$$

Thus, this equation can be directly integrated, if the perturbed Hamiltonian is known.

Hence the new wave function is known and we can calculate the behavior of the system from this new wave function.

$$|\Psi\rangle = e^{-iE_n t/\hbar} |\psi_n\rangle + \sum_n C_n^{(1)}(t) e^{-iE_n t/\hbar} |\psi_n\rangle$$

For the second order

$$C_m^{(2)}(t) = (i\hbar)^{-2} \sum_n C_n^{(1)}(t) e^{-i\omega_{nm}t} H^1_{mn} \dots \dots (3)$$

For the higher order (*S'th*) of perturbation, the expansion coefficient becomes,

$$i\hbar \dot{C}_m^{(s+1)}(t) = \sum_n C_n^{(s)}(t) e^{-i\omega_{nm}t} H^1_{mn}$$

$s = 0, 1, 2, \dots$ order of perturbation.

Here, H^1 is the perturbed Hamiltonian in matrix form $\langle \psi_n(r) | H^1 | \psi_m(r) \rangle$.

The equation (3) is the set of coupled differential equations for $C_m^{(s)}(t)$.

The matrix element $\langle \psi_n(r) | H^1 | \psi_m(r) \rangle$ is non zero, and thus we will use the selection rule by which all the matrix elements for given perturbation vanish, except for a few "select" ones characterized by special changes in the quantum numbers.

We now consider a hydrogen atom, and then expose this system to an electric field treated classically in dipole approximation. The electric field alters the Hamiltonian of the initial system, which in turn alters the corresponding Eigen-energies and Eigen-states. Perturbation theory allows us to find approximate solutions to the perturbed Eigen-value problems by beginning with the known exact solutions of the unperturbed problems and then making small corrections to be based on the new perturbing potential.

Then, the perturbation part of the Hamiltonian is

$$H^1 = -\sum_j E_0 e^{-i(\omega + \delta_j)t} \hat{\epsilon}_j \cdot r \dots \dots \dots (4)$$

Where, ω is the angular frequency of the external radiation and δ_j the phase difference between different beams and $\hat{\epsilon}_j$ represent polarization vector of the different beams are propagating along the same direction.

Now, we have evaluated the transition between the continuum states of two Eigen states $|g\rangle$ as initial state for (t=0) and $|f\rangle$ as final states at later time t.

$$\text{Let, } \hbar\omega_0 = E_f - E_g,$$

where, ω_0 is the frequency of the transition between two states.

$\hbar\omega_0 > 0$ means atom has absorbed the photon,

$\hbar\omega_0 < 0$ means atom has emitted the photon.

Plugging equation (4) into equation (1) after performing t integral (Shrestha *et al.* 2011)

$$C_f^{(1)}(t) = E_0 \langle f | \hat{\epsilon}_i \cdot r | g \rangle \left[\frac{e^{i(\omega_0 + \omega)t} - 1}{(\omega_0 + \omega)} + \frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} \right]$$

Let the external frequency ω , be nearly equal to the transition frequency ω_0 . Then the second term in the above equation becomes arbitrarily large with respect to the first. Still for the fixed time t and H(t), since we cannot have $C_f(t) \gg 1$. We choose sufficiently small amount of time such that our perturbation expansion works even when ω is almost equal to ω_0 . Thus, we can neglect the first term giving

$$C_f^{(1)}(t) \approx E_0 \langle f | \hat{\epsilon}_i \cdot r | g \rangle \left[\frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} \right]$$

The probability of atom at time t is

$$P_f = |C_f^{(1)}(t)|^2 = E_0^2 \left| \langle f | \hat{\epsilon}_i \cdot r | g \rangle \left[\frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} \right] \right|^2$$

Using the identity operator,

$$|e^{i\theta} - 1|^2 = 2(1 - \cos\theta) = 4\sin^2 \theta / 2$$

Hence, the probability at time t is,

$$P_f(t) = E_0^2 \left| \langle f | \hat{\epsilon}_i \cdot r | g \rangle \right|^2 \frac{\sin^2[(\omega_0 - \omega)t / 2]}{(\omega_0 - \omega)^2}$$

The transition rate

$$\Gamma^{(1)} = E_0^2 \left| \langle f | \hat{\epsilon}_i \cdot r | g \rangle \right|^2 \delta(\omega_0 - \omega)$$

The first order correction gives the ordinary, linear optical properties of material.

For second order correction

$$C_n^{(2)}(t) = \int_0^t dt \sum_n C_n^{(1)}(t) e^{-i(\omega_n - \omega)t} H_{fn}$$

$$= \int_0^t dt E_0 \langle n | \hat{\epsilon}_i \cdot r | g \rangle \times \left[\frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} \right] e^{-i(\omega_n - \omega)t} H_{fn}$$

Here, $\hbar\omega_0 = E_n - E_g = \hbar\omega_{ng}$

$$C_f^{(2)}(t) = E_0^2 \frac{1}{(\omega_0 - \omega)} \langle f | \hat{\epsilon}_i \cdot r | n \rangle \langle n | \hat{\epsilon}_i \cdot r | g \rangle \times \left[\frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} - \frac{e^{i(\omega_n - \omega)t} - 1}{(\omega_n - \omega)} \right]$$

The probability is

$$P_f^{(2)} = \left| E_0^2 \frac{1}{(\omega_0 - \omega)} \langle f | \hat{\epsilon}_i \cdot r | n \rangle \langle n | \hat{\epsilon}_i \cdot r | g \rangle \times \left[\frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)} - \frac{e^{i(\omega_n - \omega)t} - 1}{(\omega_n - \omega)} \right] \right|^2$$

Similarly for three photon, after performing integration,

$$C_f^{(3)}(t) = E_0^3 \langle f | \hat{\epsilon}_i \cdot r | m \rangle \langle m | \hat{\epsilon}_i \cdot r | n \rangle \langle n | \hat{\epsilon}_i \cdot r | g \rangle \times \left[\frac{e^{i(\omega_0 - \omega)t} - 1}{(\omega_0 - \omega)(\omega_n - 2\omega)(\omega_m - 3\omega)} - \frac{e^{i(\omega_m - \omega)t} - 1}{(\omega_m - \omega)(\omega_n - 2\omega)(\omega_0 - \omega)} \right]$$

The probability of atom in $|f\rangle$ at time t is

$$P_f^{(3)}(t) = \left| E_{\omega_1} E_{\omega_2} \sum_m \sum_n \frac{\langle f | \hat{\epsilon}_1 \cdot r | m \rangle \langle m | \hat{\epsilon}_2 \cdot r | n \rangle \langle n | \hat{\epsilon}_3 \cdot r | g \rangle}{(\omega_m - \omega)(\omega_n - 2\omega)} \times \left[\frac{e^{i(\omega_1 + 2\omega)t} - 1}{(\omega_1 + 2\omega)} \right] \right|^2$$

The transition rate for multiple beams j, k and l , can be expressed as

For first order correction

$$\Gamma_f^{(1)} \approx E_{\omega_1}^2 |\langle f | \hat{\epsilon}_1 \cdot r | g \rangle|^2$$

For two and three photons

$$\Gamma_f^{(2)} \approx E_{\omega_1}^2 E_{\omega_2}^2 \left| \sum_n \langle f | \hat{\epsilon}_1 \cdot r | n \rangle \langle n | \hat{\epsilon}_2 \cdot r | g \rangle \left[\frac{1}{(\omega_n - \omega)} \right] \right|^2$$

$\Gamma_f^{(3)} \approx$

$$E_{\omega_1}^2 E_{\omega_2}^2 E_{\omega_3}^2 \left| \sum_m \sum_n \langle f | \hat{\epsilon}_1 \cdot r | m \rangle \langle m | \hat{\epsilon}_2 \cdot r | n \rangle \langle n | \hat{\epsilon}_3 \cdot r | g \rangle \left[\frac{1}{(\omega_m - \omega)(\omega_n - 2\omega)} \right] \right|^2$$

The calculation of ionization rate has been reducing to a matter of evaluating matrix element.

Let us denote the matrix element of the form by M as

For first order correction

$$M_f^{(1)} \approx \langle f | \hat{\epsilon}_1 \cdot r | g \rangle$$

For second order correction

$$M_f^{(2)} \approx \left[\frac{\sum_n \langle f | \hat{\epsilon}_1 \cdot r | n \rangle \langle n | \hat{\epsilon}_2 \cdot r | g \rangle}{(\omega_n - \omega)} \right] \dots \dots (5)$$

For third order correction

$$M_f^{(3)} \approx \left[\frac{\sum_m \sum_n \langle f | \hat{\epsilon}_1 \cdot r | m \rangle \langle m | \hat{\epsilon}_2 \cdot r | n \rangle \langle n | \hat{\epsilon}_3 \cdot r | g \rangle}{(\omega_m - \omega)(\omega_n - 2\omega)} \right] \dots (6)$$

Dalgarno and Lewis (Dalgarno *et al.* 1956) developed a simple and practical method to solve perturbation equations; the method was later adopted by many authors to tackle a variety of problems. This method (Francisco 1952) consists of writing the perturbation correction to the Eigenfunction as

$$\Psi_p(r) = F_p(r) \Psi_0(r), \quad p = 0, 1, 2, \dots$$

And solving the resulting equations, the Dalgarno operator $F_p(r)$ thus becomes,

$$-\frac{1}{2} \nabla^2 F_p - \frac{1}{\Psi_0} \nabla \Psi_0 \cdot \nabla F_p + V F_p - \sum_{q=0}^{p-1} E_q F_p = 0$$

In this equation, ∇ is the gradient vector operator and the dot stand for the standard scalar product. These equations are easier to solve than the original differential equation for the perturbation corrections. In

many cases the correction factors F_p are simple polynomial function of the coordinates. For $F_0 = 1$ is suitable solution to the equation of order zero, and E_0 does not appear in the perturbation equation. The Dalgarno–Lewis method (Nandi *et al.* 1996) allows us to calculate the perturbation series to higher orders for non degenerate states. The method is based on conversion of Eigen value problem into series of inhomogeneous differential equation. These equations determine successively the correction to the Eigen function and the energy correction are obtained by simple expectation value (Schiff 1968).

In our calculations as shown in equation (5) and equation (6), we have assumed two auxiliary dimensionless operators for two photons as F_j , and G_{jk} for three photons, where j, k are the number of beams having same frequency, but different polarization vectors propagating along the same direction.

Equation(5) is evaluated by defining F_j , such as

$$\begin{aligned} (\hat{\epsilon}_j \cdot \vec{r}) |g\rangle &= [F_j H_0 - H_0 F_j + \omega F_j] |g\rangle \\ (\hat{\epsilon}_j \cdot \vec{r}) \psi &= [F_j H_0 - H_0 F_j + \omega F_j] \psi \end{aligned}$$

Now, the equation (5) becomes,

$$M_0^{(2)} = \langle f | (\hat{\epsilon}_i \cdot \vec{r}) F | g \rangle$$

$$\text{Here, } H_0 = -\frac{1}{2} \nabla^2 - \frac{1}{r}$$

Thus, $(\hat{\epsilon}_i \cdot \vec{r}) \psi$

$$= \frac{\nabla F}{2} \psi + \nabla F_i \cdot \nabla \psi + \omega F \psi \dots (7)$$

Similarly for three photon ionization, we define G_0 such as,

$$(\hat{\epsilon}_i \cdot \vec{r}) F_i | g \rangle = [G_0 H_0 - H_0 G_0 + \omega G_0] | g \rangle$$

Then equation (6) becomes,

$$M_0^{(3)} = \langle f | (\hat{\epsilon}_i \cdot \vec{r}) G_0 | g \rangle$$

$$(\hat{\epsilon}_i \cdot \vec{r}) F_i \psi$$

$$= \frac{\nabla G_0}{2} \psi + \nabla G_0 \cdot \nabla \psi + \omega G_0 \psi \dots (8)$$

In general for the higher order, this can be done by defining a set of $n-1$ operators F_n with $n = 1, 2, \dots, n-1$ such as (Delone 1999).

$$(\hat{\epsilon}_i \cdot \vec{r}) F_{n-1} | g \rangle = (F_n H_0 - H_0 F_n + n \omega F_n) | g \rangle$$

In hydrogen atom, the electron potential is the well known spherically symmetric coulomb potential, owing to the spherically symmetric, it is very convenient to solve TDSE in spherical coordinates (Griffiths 1999).

$$\text{Let } F_i = (\hat{\epsilon}_i \cdot \vec{r}) f(\omega, r)$$

Where, $(\hat{\epsilon}_i \cdot \vec{r})$ is the angular part given by Legendre polynomial and unknown $f(\omega, r)$ simply as f is the radial part.

After a few manipulations the differential equation for two photon ionization takes the form,

$$r f'' + (4 - 2r) f' + (2\omega r - 2) f = 2r$$

Similarly for three photon, after assuming

$$G_{ijk} = \left[\frac{3}{2} \hat{\epsilon}_i \cdot \vec{r} \hat{\epsilon}_k \cdot \vec{r} - \frac{1}{2} \hat{\epsilon}_i \cdot \hat{\epsilon}_k r^2 \right] g_2 + \hat{\epsilon}_j \cdot \hat{\epsilon}_k g_1$$

Then after some algebra, we can have the simple differential equation as

$$r g_0'' + (2 - 2r) g_0' + 4\omega r = \frac{2}{3} r^3 f$$

$$r g_2'' + (6 - 2r) g_2' + (4\omega r - 4) g_2 = \frac{4}{3} r f$$

Here we have used the method of Laplace transform (Ince 1956) for the solution of this differential equation (Radhakrishnan *et al.* 2004).

$$\Phi(p, q, \lambda, t, r) = \int ds e^{-st} K(p, q, \lambda, s)$$

$$K(p, q, \lambda, s) = \left(\frac{1-\lambda}{1+\lambda} \right)^p (s+\lambda)^{-q} (s-\lambda)^{-p}$$

Finally, we can have $f(r)$, as

$$f(r) = \frac{1}{\omega} - \frac{1}{2\omega} \Phi(1, 1, \lambda, 1, r)$$

$$g_2(r) = \frac{1}{3\omega} - \frac{1}{3\omega} \Phi(1, 1, \lambda, 1, r) + \frac{2}{3\omega} \int_0^t dt \frac{K(1, 1, \lambda, 1, t)}{K(3, 3, \lambda, t)} \Phi(2, 2, \lambda, t, r)$$

where $\lambda = \sqrt{(1 - 2\omega)}$ and $\lambda = \sqrt{(1 - 4\omega)}$

$$g_0(r) = \frac{2}{3\omega} \left[\frac{r^2}{4} + \frac{1}{4\omega^2} (1 - 2\lambda) - \frac{3}{8\omega} \right]$$

$$- \frac{1}{3\lambda\omega} \Phi(0, 0, \lambda, t, r)$$

$$- \frac{1}{6\omega} \left[r^2 + \frac{\lambda}{\omega} r - \frac{1}{\omega} \left(1 + \frac{1}{\lambda} \right) \right] \Phi(1, 1, \lambda, 1, r)$$

$$- \frac{1}{3\omega} \left(1 + \frac{1}{\lambda} \right) \int_0^t dt \frac{K(1, 1, \lambda, 1, t)}{K(1, 1, \lambda, t)}$$

$$\times \left[\frac{1 - 2\omega}{\omega(1 + \lambda)} - \frac{t}{\omega} - \frac{2}{t + \lambda} + \frac{2}{(t + \lambda)^2} \right] \times$$

$$\Phi(0, 0, \lambda, t, r)$$

Results and Discussion

The idea of DL method is to define an auxiliary operator such that the evaluation of intermediate sum is not

needed. Now, the difficulties associated with the infinite summation is reduced to the problem of finding an appropriate expressions for the operators F_i and G_i .

We have explored the technique of evaluating higher-order perturbation theory for the multiple beams of same frequency but different polarization from the point of view of Schrodinger's differential equation. The method seems very well adaptable for the problems such as that of the hydrogen atom (Charles 1959).

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