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Feynman diagram approach to atomic collisions*

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Abstract. A quantum field theoretic formulation of atomic collision phenomena involving non-relativistic free and bound systems is developed and a calculational procedure in terms of Feynman diagrams is prescribed. Matrix elements of several atomic collision processes have been calculated. In most cases standard quantum mechanical results are reproduced. But in some cases new terms appear in the scattering matrix whose contribution though negligibly small in the low energy region, become important at higher energies.

Keywords. Non-relativistic field theory; Feynman rules; charge form-factor of an atom; Kramers-Heisenberg formula; Van der Waals interaction.

1. Introduction

In the Feynman diagram approach to atomic collision problems developed earlier (Pradhan and Khare 1976), the Bethe-Salpeter method was used to obtain the vertex function involving the atom and its constituents while standard expressions were used for propagators. This method was adequate for some collisions involving hydrogen-like atoms. For some other collisions involving hydrogen-like atoms and collisions involving three-body bound states, this method is not applicable. It is the purpose of the present paper to develop a Hamiltonian approach within the framework of quantum field theory for the interaction among the non-relativistic bound systems involving two particles and their constituents and their interactions with photons. From this, Feynman diagrams and the rules for writing down the corresponding S-matrix elements would follow quite naturally.

The problem that one would encounter in perturbation theory for scattering of particles that can form bound states is that such states would not come out of the theory unless these are used as inputs. For instance in nonrelativistic electron-proton collision, it would be necessary to put hydrogen atom, in addition to electron and proton, into the Hamiltonian before doing perturbative calculations for scattering processes. A familiar example from particle physics may be useful. In the problem of collision between a pion and a nucleon, a resonance occurs around pion laboratory energy of 200 MeV. A successful perturbation theory of pion-nucleon collision phenomena must, therefore, use this resonant state as an input in the Hamiltonian.

Having made our point that the bound entity must be used as input, the task of implementing the same has to be undertaken. For this let us first consider the

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simplest of all atomic systems: the hydrogen atom. Our task is to write down a Hamiltonian in terms of the field operators of the proton, the electron and the hydrogen atom from which matrix elements of any process involving these three 'particles' can be calculated. This will be done in §2. §3 will be devoted to obtain rules for writing down S-matrix elements for Feynman diagrams for any scattering process and §4 will be devoted for the actual calculation of matrix elements of simple processes. Interaction of the above system with photon and application to the scattering of photon by hydrogen atom are discussed in §5.

Apart from obtaining standard quantum mechanical results we do get some entirely new results. For example, in addition to diagrams in photon-atom collision which yield the Kramers-Heisenberg formula, there are diagrams whose contribution, although negligible in the low energy region, is comparable to the Kramers-Heisenberg terms at sufficiently high energy.

2. Non-relativistic field theory

As stated earlier we shall consider the simplest non-relativistic system of a proton, an electron and a hydrogen atom interacting with each other. We introduce a second quantised field operator $h(\vec{x}_1, \vec{x}_2, t)$ for the hydrogen atom where $\vec{x}_1$ is the coordinate of the proton and $\vec{x}_2$ is that of the electron. The Hamiltonian of the system can be written as

$$H = H_0 + H_{\text{int}} = H_h + H_p + H_e + H_{\text{int}}, \tag{1}$$

where

$$H_h = \iint\limits_{t_1 = t_2 = t} d^3 x_1 \, d^3 x_2 \left[\frac{1}{2M} (\vec{\nabla}_1 h^\dagger)(\vec{\nabla}_1 h) + \frac{1}{2m} (\vec{\nabla}_2 h^\dagger) \cdot (\vec{\nabla}_2 h) + v(|\vec{x}_2 - \vec{x}_1|) h^\dagger h \right] \tag{2}$$

is the Hamiltonian of the hydrogen atom whose second quantised field operator $h(\vec{x}_1, \vec{x}_2, t)$ is represented by

$$h(\vec{x}_1, \vec{x}_2, t) = h(\vec{X}, \vec{x}, t) = \sum_{\text{nlm}} \int \frac{d^3 P}{(2\pi)^3} a_{\text{nlm}}(\vec{P}) \, u_{\text{nlm}}(\vec{x}) \exp\left[(i \vec{P} \cdot \vec{X} - i \left(\frac{P^2}{2(M+m)} - \epsilon_n \right) t \right] \tag{3}$$

where

$$\vec{X} = \frac{M \vec{x}_1 + m \vec{x}_2}{M + m};$$

$\vec{x} = \vec{x}_2 - \vec{x}_1$ being the centre of mass and relative coordinates respectively. $u_{\text{nlm}}(\vec{x})$

and $a_{\mathrm{nlm}}(\vec{P})$ being the hydrogen atom wavefunction and annihilation operator satisfying commutation relation

$$[a_{\mathrm{nlm}}(\vec{P}), a^{\dagger}_{\mathrm{n'l'm'}}(\vec{P'})] = \delta_{\mathrm{nn'}}\,\delta_{\mathrm{ll'}}\,\delta_{\mathrm{mm'}}\,\delta(\vec{P}-\vec{P'}), \tag{4}$$

$$H_p = \frac{1}{2M}\int d^3x\,\vec{\nabla}p^{\dagger}(\vec{x},t)\cdot\vec{\nabla}p(\vec{x},t), \tag{5a}$$

and

$$H_e = \frac{1}{2m}\int d^3x\,\vec{\nabla}e^{\dagger}(\vec{x},t)\cdot\vec{\nabla}e(\vec{x},t) \tag{5b}$$

are Hamiltonians for the proton and the electron and

$$\begin{aligned} H_{\mathrm{int}} = \iint_{t_1=t_2=t} & d^3x_1\,d^3x_2\,v(|\vec{x}_2-\vec{x}_1|)\,[h^{\dagger}(\vec{x}_1,\vec{x}_2,t)\,p(\vec{x}_1,t)\,e(\vec{x}_2,t) \\ & + p^{\dagger}(\vec{x}_1,t)\,e^{\dagger}(\vec{x}_2,t)\,h(\vec{x}_1,\vec{x}_2,t) + p^{\dagger}(\vec{x}_1,t)\,p(\vec{x}_1,t)\,e^{\dagger}(\vec{x}_2,t)\,e(\vec{x}_2,t) \\ & - p^{\dagger}(\vec{x}_1,t)\,p(\vec{x}_1,t)\,p^{\dagger}(\vec{x}_2,t)\,p(\vec{x}_2,t) - e^{\dagger}(\vec{x}_1,t)\,e(\vec{x}_1,t) \\ & e^{\dagger}(\vec{x}_2,t)\,e(\vec{x}_2,t)] \end{aligned} \tag{6}$$

is the interaction Hamiltonian which contains, besides proton-proton, electron-electron and proton-electron interactions, terms $h^{\dagger}\,p\,e$ and $p^{\dagger}\,e^{\dagger}\,h$ which represent virtual conversion of the hydrogen atom into its constituents i.e., proton and electron. It is similar to the $N^*\,N\pi$ interaction in pion-nucleon collision problem. The non-relativistic field operators $p(x)$ and $e(x)$ are essentially annihilation operators i.e.

$$\begin{aligned} p(x) &= \frac{1}{(2\pi)^3}\sum_k c_k \exp(ikx), & [c_k, c^{\dagger}_{k'}] &= \delta_{kk'}, \\ e(x) &= \frac{1}{(2\pi)^3}\sum_k b_k \exp(ikx), & [b_k, b^{\dagger}_{k'}] &= \delta_{kk'} \end{aligned} \tag{7}$$

It will be seen that the equation of motion resulting from H_h is

$$-\left[\frac{1}{2M}\nabla_1^2 + \frac{1}{2m}\nabla_2^2 - v(|\vec{x}_2-\vec{x}_1|)\right]h(\vec{x}_1,\vec{x}_2,t) = i\frac{\partial h(\vec{x}_1,\vec{x}_2,t)}{\partial t} \tag{8}$$

which is the Schrödinger equation for the hydrogen atom. Use has been made of the equal time commutation relation

$$\begin{aligned} & [h(x_1,x_2), h^{\dagger}(x_1',x_2')] = \delta(\vec{x}_1-\vec{x}_1')\,\delta(\vec{x}_2-\vec{x}_2') \\ & t_1 = t_2 = t = t_1' = t_2' \end{aligned} \tag{9}$$

and the Heisenberg equation

$$[H_h, h(\vec{x}_1, \vec{x}_2, t)] = i \frac{\partial h(\vec{x}_1, \vec{x}_2, t)}{\partial t} \tag{10}$$

in obtaining the above Schrödinger equation, if we use the separability ansatz:

$$h(\vec{x}_1, \vec{x}_2, t) = h(\vec{X}, \vec{x}, t) = \sum_n \Phi_n(\vec{X}, t)\, u_n(\vec{x}) \tag{11}$$

with $\Phi_n(\vec{X}, t)$ as a second quantised field and $u_n(\vec{x})$ as the c-number energy eigenfunction, the Hamiltonian H_h given by (2) simplifies to

$$H_h = \sum_n \int d^3X \left[\frac{\vec{\nabla}\Phi_n^\dagger(\vec{X}, t) \cdot \vec{\nabla}\Phi_n(\vec{X}, t)}{2(M+m)} - \epsilon_n \Phi_n^\dagger(\vec{X}, t)\Phi_n(\vec{X}, t) \right] \tag{12}$$

and the Schrödinger equation (8) separates into

$$-\frac{\nabla^2 u_n(\vec{x})}{2\mu} + v(x)\, u_n(\vec{x}) = -\epsilon_n u_n(\vec{x}), \tag{13a}$$

and

$$-\frac{\nabla^2 \Phi_n(\vec{X}, t)}{2(M+m)} - \epsilon_n \Phi_n(\vec{X}, t) = i \frac{\partial \Phi_n(\vec{X}, t)}{\partial t}. \tag{13b}$$

Equation (13b) is also obtained from (12) using Heisenberg equation of motion for $\Phi_n(\vec{X}, t)$ and the commutation relation

$$[\Phi_n(\vec{X}, t), \Phi_{n'}^\dagger(\vec{X}', t)] \equiv \delta_{nn'}\, \delta(\vec{X} - \vec{X}'). \tag{14}$$

It should be noted that although $\Phi_n(\vec{X}, t)$ is a function of the centre of mass co-ordinate, its Schrödinger equation (13b) contains the energy of relative motion ϵ_n. It can, therefore, be the field for hydrogen atom. The interaction Hamiltonian can now be expressed in terms of centre of mass co-ordinates. For this we rewrite (7) as

$$p(\vec{x}_1, t) = \sum_{\vec{k}} \frac{c_k(\vec{X}, t)}{(2\pi)^3} \exp(ib\vec{k} \cdot \vec{x}), \quad b = \frac{m}{M+m},$$

$$e(\vec{x}_2, t) = \sum_{\vec{q}} \frac{b_q(\vec{X}, t)}{(2\pi)^3} \exp(-ia\vec{k} \cdot \vec{x}), \quad a = \frac{M}{M+m} \tag{15}$$

and use (11) in (6) and obtain

$$H_{\text{int}} = \sum_n \sum_{\vec{k}, \vec{q}} \Gamma_n(b\vec{k} - a\vec{q}) \int d^3X [\Phi_n^\dagger(\vec{X}, t)\, c_{\vec{k}}(\vec{X}, t) b_{\vec{q}}(\vec{X}, t)$$

$$+ b^{\dagger}_{\vec{q}}(\vec{X},t)C^{\dagger}_{\vec{k}}(\vec{X},t)\Phi_n(\vec{X},t)] + \sum_{\substack{\vec{k},\vec{k}'\\ \vec{q},\vec{q}'}} v\{b(\vec{k}'-\vec{k}) - a(\vec{q}'-\vec{q})\}$$

$$\int d^3X [c^{\dagger}_{\vec{k}}(\vec{X},t)C_{\vec{k}'}(\vec{X},t)b^{\dagger}_{\vec{q}}(\vec{X},t)b_{\vec{q}'}(\vec{X},t)$$

$$- c^{\dagger}_{\vec{k}}(\vec{X},t)\, c_{\vec{k}'}(\vec{X},t)\, c^{\dagger}_{\vec{q}}(\vec{X},t)\, c_{\vec{q}}(\vec{X},t) - b^{\dagger}_{\vec{k}}(\vec{X},t)b_{\vec{k}'}(\vec{X},t)$$

$$b^{\dagger}_{\vec{q}}(\vec{X},t)b_{\vec{q}}(\vec{X},t)], \tag{16}$$

where $$\Gamma_n(\vec{K}) = \int d^3x \exp(i\vec{K}\cdot\vec{x})\, v(x)\, u_n(\vec{x}), \tag{17}$$

is the vertex function for the hydrogen-proton-electron vertex. The propagator for the fields $\Phi_n(\vec{X},t)$, $C_{\vec{k}}(\vec{X},t)$ and $b_{\vec{q}}(\vec{X},t)$ and their Fourier components can now be obtained using

$$\Phi_n(\vec{X},t) = \sum_{\vec{P}} (2\pi)^{-3} a_n(\vec{P}) \exp(i\vec{P}\cdot\vec{X} - iE_n t), \tag{18a}$$

$$c_{\vec{k}}(\vec{X},t) = c(\vec{k}) \exp\left(i\vec{k}\cdot\vec{X} - i\frac{k^2 t}{2M}\right), \tag{18b}$$

$$b_{\vec{q}}(\vec{X},t) = b(\vec{q}) \exp\left(i\vec{q}\cdot\vec{X} - i\frac{q^2 t}{2m}\right) \tag{18c}$$

where

$$E_n = \frac{P^2}{2(M+m)} - \epsilon_n$$

as can be seen by substituting (18a) in (13b). It is then clear that the propagators for the centre of mass motion of the hydrogen atom, $\mathcal{G}_n(\vec{P},P_0)$, that of the proton, $\Delta_p(\vec{k},k_0)$ and for the electron, $\Delta_e(\vec{q},q_0)$ are:

$$\mathcal{G}_n(\vec{P},P_0) = -i\int d^3X \int_{-\infty}^{+\infty} dt\, \langle 0|(\Phi_n(\vec{X},t)\,\Phi_n^{\dagger}(\vec{0},0))_+|0\rangle$$

$$\exp(-i\vec{p}\cdot\vec{X} + iP_0 t)$$

$$= \left[P_0 - \frac{P^2}{2(M+m)} + \epsilon_n + i\eta\right]^{-1}. \tag{19a}$$

$$\Delta_p(\vec{k},k_0) = -i\int_{-\infty}^{+\infty} dt\, \langle 0|(c_{\vec{k}}(t)\, c^{\dagger}_{\vec{k}}(0))_+|0\rangle \exp(-ik_0 t)$$

$$= \left[k_0 - \frac{k^2}{2M} + i\eta\right]^{-1} \tag{19b}$$

$$\Delta_e(\vec{q},q_0) = -i\int_{-\infty}^{+\infty} dt\, \langle 0|(b_{\vec{q}}(t)\, b^{\dagger}_{\vec{q}}(0))_+|0\rangle$$

$$= \left[q_0 - \frac{q^2}{2m} + i\eta\right]^{-1}. \tag{19c}$$

3. Feynman rules

We are now in a position to write down the rules for Feynman diagrams for the S-matrix elements defined by

$$S = 1 - i\int_{-\infty}^{+\infty} dt_1\, H_{\text{int}}(t_1) + \frac{(-i)^2}{2!}\int_{-\infty}^{+\infty} dt_1 \int_{-\infty}^{+\infty} dt_2\, (H_{\text{int}}(t_1)\, H_{\text{int}}(t_2))_+ + \ldots + \frac{(-i)^n}{n!}\int_{-\infty}^{+\infty} dt_1 \ldots \int_{-\infty}^{+\infty} dt_n\, (H_{\text{int}}(t_1)\ldots H_{\text{int}}(t_n))_+ + \ldots \tag{20}$$

These are

(i) Draw thick lines for bound states such as hydrogen atom and thin lines for constituents such as protons and electrons with arrows representing directions of their momenta. Since all "particles" obey non-relativistic dynamics, there are no arrows pointing backwards.

(ii) Draw a dotted line for each $v(\vec{k})$ appearing in the interaction Hamiltonian and label it by momentum $\vec{k}$ and zero energy. The point where this line joins either a proton or an electron is to be treated as a simple vertex.

(iii) Conserve energies and momenta at each vertex. Write $\Gamma_n(b\vec{k} - a\vec{q})$ for each hydrogen-proton-electron vertex, $\vec{k}$ being the proton momentum and $\vec{q}$ being that of the electron. All simple vertices are to be represented by unity.

(iv) Write down appropriate propagators for the internal lines.

(v) Affix an overall factor $i/(2\pi)^4$ for each loop in the diagram.

(vi) Integrate over the independent energy and momenta of internal lines.

4. Calculation of simple processes

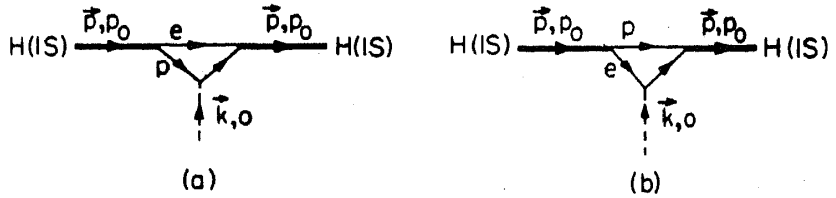
4.1. *Charge form-factor of an atom*

We can obtain the charge distribution of the hydrogen atom using the Feynman diagram technique. There are two diagrams for the charge form-factor. These are given in figures 1(a) and 1(b). The former gives the proton charge distribution while the latter gives the electron charge distribution. The net charge distribution is the sum of the two. The matrix elements give the Fourier transforms of the charge distribution and are

$$\tilde{\rho}_p(\vec{k}) = e\int \frac{d^3q}{(2\pi)^3}\, g_p^{(1S)}(\vec{q} - b\vec{k})\, g_p^{(1S)}(\vec{q}), \tag{21a}$$

and

$$\tilde{\rho}_e(\vec{k}) = -e\int \frac{d^3q}{(2\pi)^3}\, g_e^{(1S)}(\vec{q} - a\vec{k})\, g_e^{(1S)}(\vec{q}). \tag{21b}$$



Figures 1(a) and 1(b). Feynman diagrams for charge form-factor of hydrogen atom.

In configuration space, these become

$$\rho_p(\vec{r}) = \frac{e}{\pi\left(\frac{ma_0}{M+m}\right)^3}\exp\left(-\frac{2(M+m)}{m}\frac{r}{a_0}\right) \approx \left(\frac{M}{m}\right)^3\frac{e}{\pi a_0^3}$$
$$\exp(-2Mr/ma_0), \tag{22a}$$

$$\rho_e(\vec{r}) = -\frac{e}{\pi\left(\frac{Ma_0}{M+m}\right)^3}\exp\left(-\frac{2(M+m)}{m}\frac{r}{a_0}\right) \approx -\frac{e}{\pi a_0^3}\exp(-2r/a_0) \tag{22b}$$

and hence

$$\rho(\vec{r}) = \rho_p(\vec{r}) + \rho_e(\vec{r}) = \frac{e}{\pi a_0^3}[(M/m)^3\exp(-2Mr/ma_0) - \exp(-2r/a_0)]. \tag{23}$$

This shows that whereas the positive charge is confined to a sphere of radius ma_0/M, the negative charge is contained within a sphere of radius a_0.

If we consider a bound state of two equal mass particles such as the nonrelativistic positronium, the charge distribution that would follow from equation (23) is $\rho(\vec{r}) = 0$ which means that such a bound state is completely neutral. This is in keeping with the fact that such a particle is an eigenstate of the charge conjugation operator. It may be worth noting here that η and π° which are considered to be a bound state of quarks of equal mass but opposite charge will also be truly neutral, i.e., charge density will be zero everywhere. This will not be the case with the neutral K meson. While the K° meson consisting of $\bar{s}$ and d quarks will have positively charged central core surrounded by negatively charged outer layer because of higher mass of strange quark, the $\bar{K}^\circ$ will have just the opposite charge distribution.

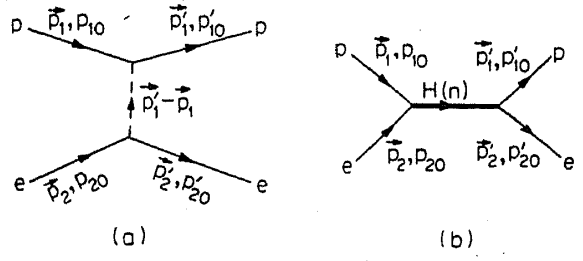
4.2 *Proton-electron scattering*

Next we consider proton-electron scattering. For this, there are two diagrams given in figures 2(a) and 2(b), whose matrix elements, according to rules enumerated above, are

$$M_a = v(\vec{p}_1' - \vec{p}_1) = -\frac{4\pi e^2}{|\vec{p}_1 - \vec{p}_1'|^2} \tag{24a}$$

and

$$M_b = \sum_n \frac{\Gamma_n(b\vec{p}_1 - a\vec{p}_2)\,\Gamma_n(b\vec{p}_1' - a\vec{p}_2')}{\frac{p_1^2}{2M} + \frac{p_2^2}{2m} - \frac{(\vec{p}_1+\vec{p}_2)^2}{2(M+m)} + \epsilon_n + i\eta} \tag{24b}$$



Figures 2(a) and 2(b). Feynman diagrams for proton-electron scattering.

It will be seen that M_a as it is and M_b in the limit of $m/M \to 0$ agree with standard quantum mechanical results (Dirac 1947).

4.3 *Proton-hydrogen atom scattering*

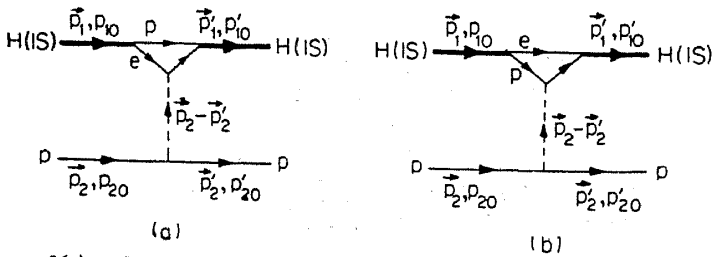
Since the hydrogen atom is electrically neutral, it cannot directly interact with the proton. It must first break up into virtual proton and electron states which, after interacting with the external proton, recombine to give in figures 3(a) and 3(b). The corresponding matrix elements are,

$$\frac{e^2 i}{-\vec{p}_1|^2} \int \frac{d^3q}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{dq_0}{2\pi}$$

$$\frac{\Gamma_0(\vec{q}-b\vec{p}_1)\,\Gamma_0(\vec{q}-b\vec{p}_1')}{-\frac{q^2}{\gamma m_1}\Big)\left\{\frac{p_1^2}{2(M+m)} - \epsilon_0 - q_0 - \frac{(\vec{p}_1-\vec{q})^2}{2M}\right\}\left\{\frac{p_1'^2}{2(M+m)} - \epsilon_0 - q_0 - \frac{(\vec{p}_1'-\vec{q})^2}{2M}\right\}} \tag{25a}$$

$$\int \frac{d^3q}{(2\pi)^3} \int_{-\infty}^{+\infty} \frac{dq_0}{2\pi}$$

$$\frac{\Gamma_0(\vec{q}-a\vec{p}_1)\,\Gamma_0(\vec{q}-a\vec{p}_1')}{\frac{p_1^2}{2(M+m)} - \epsilon_0 - q_0 - \frac{(\vec{p}_1-\vec{q})^2}{2m}\Big\}\Big\{\frac{p_1'^2}{2(M+m)} - \epsilon_0 - q_0 - \frac{(\vec{p}_1'-\vec{q})^2}{2m}\right\}} \tag{25b}$$



Figures 3(a) and 3(b). Feynman diagrams for potential scattering between proton and hydrogen atom.

which on integration over q_0 and use of the relation

$$g_n(\vec{k}) = \frac{-\Gamma_n(\vec{k})}{k^2/2\mu + \epsilon_n}, \tag{26}$$

become $$M_a = -\frac{4\pi e^2}{Q^2}\int \frac{d^3q}{(2\pi)^3} g_0(\vec{q})\, g_0(\vec{q} - b\vec{Q}), \tag{27a}$$

and $$M_b = \frac{4\pi e^2}{Q^2}\int \frac{d^3q}{(2\pi)^3} g_0(\vec{q})\, g_0(\vec{q} - a\vec{Q}), \tag{27b}$$

where $\vec{Q} = \vec{p}_1' - \vec{p}_1 = \vec{p}_2 - \vec{p}_2'$ is the momentum-transfer and

$$a = M/(M+m), \quad b = m/(M+m).$$

We obtain the potentials at the limit $m/M \to 0$ after getting the Fourier-transform of these matrix elements. These are

$$V_a = e^2/R, \tag{28a}$$

and $$V_b = e^2 s\left[-\frac{1}{sR} + e^{-sR}\left(1 + \frac{1}{sR}\right)\right] \tag{28b}$$

where $s = a_0^{-1}$, inverse of the Bohr radius, and R = separation between protons. These potentials are in agreement with the interaction between protons and the Coulomb interaction in H_2^+ — ion respectively (Pauling and Wilson 1935).

We can also consider the charge-exchange collision between proton-hydrogen atom, the only diagram representing the process is shown in figure 4. The corresponding matrix element is

$$M = -\frac{1}{2\mu}[(\vec{p}_1' - a\vec{p}_1)^2 + s^2]\, g_0(\vec{p}_1' - a\vec{p}_1)\, g_0(\vec{p}_2 - a\vec{p}_2'), \tag{29}$$

which is the same as the OBK amplitude and gives the resonance interaction in H_2^+ — ion (Pauling and Wilson 1935). From the similar diagrams for the elastic scattering and charge-exchange process between electron and hydrogen-atom, it is possible to get the Coulomb and resonance interactions in H^- — ion.

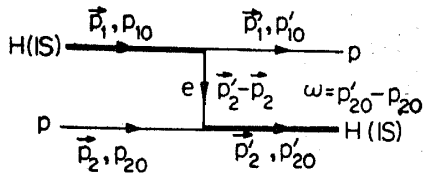


Figure 4. Feynman diagram for charge-exchange collision between proton and hydrogen atom.

5. Scattering of photon by atoms

We shall now consider the interaction of atoms with photon. Since an atom is electrically neutral, the photon cannot directly interact with it. It can, however, interact directly with its constituents through minimal coupling. This means we have to replace $\vec{\nabla}\, p\,(\vec{x}, t)$ and $\vec{\nabla}\, e\,(\vec{x}, t)$ in our Hamiltonian of § 2 by $(\vec{\nabla} + ie\,\vec{A})\, p\,(\vec{x}, t)$ and $(\vec{\nabla} - ie\,\vec{A})\, e\,(\vec{x}, t)$ respectively without making any such change for $\vec{\nabla}\, h\,(\vec{x}_1, \vec{x}_2, t)$. This results in the following additional terms to the Hamiltonians:

$$H_{\text{int}} = \frac{ie}{2M}\int\int d^3x\, dt\, [\{p\,(\vec{x}, t)\,\vec{\nabla}\, p\,(\vec{x}, t)\}\,\vec{A}\,(\vec{x}, t)$$

$$+ \{p\,(\vec{x}, t)\,\vec{\nabla}\, p^{\dagger}\,(\vec{x}, t)\}\cdot\vec{A}\,(\vec{x}, t)] - \frac{e^2}{2M}\int\int d^3x\, dt\, p^{\dagger}\,(\vec{x}, t)\, p\,(\vec{x}, t)$$

$$\vec{A}\,(\vec{x}, t)\cdot\vec{A}\,(\vec{x}, t) - \frac{ie}{2m}\int\int d^3x\, dt\, [\{e^{\dagger}\,(\vec{x}, t)\,\vec{\nabla}\, e\,(\vec{x}, t)\}\,.\,\vec{A}\,(\vec{x}, t)$$

$$+ \{e\,(\vec{x}, t)\,\vec{\nabla}\, e^{\dagger}\,(\vec{x}, t)\}\cdot\vec{A}\,(\vec{x}, t)]$$

$$- \frac{e^2}{2m}\int\int d^3x\, dt\, e^{\dagger}\,(\vec{x}, t)\, e\,(\vec{x}, t)\,\vec{A}\,(\vec{x}, t)\cdot\vec{A}\,(\vec{x}, t). \tag{30}$$

In terms of the creation and annihilation operators of the proton, electron and the photon, the last being defined by

$$\vec{A}\,(\vec{x}, t) = \sum_{\vec{k}} \frac{A_{\vec{k}}}{(2\pi)^3}\,\frac{\vec{e}_{\lambda}\,(k)}{\sqrt{2\omega}}\exp\,[i\,(\vec{k}\cdot\vec{x} - \omega t)] + \text{h.c.}, \tag{31}$$

the interaction Hamiltonian takes the following form

$$H_{\text{int}} = -\frac{e}{2M\,(2\omega)^{1/2}}\sum_{\vec{q},\,\vec{q}',\,\vec{k}}\delta\,(\vec{q} - \vec{q}' + \vec{k})\,\delta\left(\frac{q^2}{2M} - \frac{q'^2}{2m} + \omega\right)$$

$$[\{c^{\dagger}\,(\vec{q}')\,\vec{p}_{\text{op}}\,c\,(\vec{q})\}\cdot\vec{e}_{\lambda}(k)\,A_{\vec{k}} + \{c\,(\vec{q})\,\vec{p}_{\text{op}}\,c^{\dagger}\,(\vec{q}')\}\cdot\vec{e}_{\lambda}(k)\,A_{\vec{k}}]$$

$$- \frac{e^2}{4\,M\,(\omega\omega')^{1/2}}\sum_{\substack{\vec{q},\,\vec{q}'\\ \vec{k},\,\vec{k}'}}\delta\,(\vec{q} + \vec{k} - \vec{q}' - \vec{k}')\,\delta\left(\frac{q^2}{2M} + \omega - \frac{q'^2}{2M} - \omega'\right)$$

$$c^{\dagger}\,(\vec{q}')\,c\,(\vec{q})\,A^{\dagger}_{\vec{k}'}\,A_{\vec{k}}\,\vec{e}_{\lambda'}\,(k')\cdot\vec{e}_{\lambda}\,(k) + \frac{e}{2\,m\,(2\,\omega)^{1/2}}\sum_{\vec{l},\,\vec{l}',\,\vec{k}}\delta\,(\vec{l} - \vec{l}' + \vec{k})$$

$$\delta\left(\frac{l^2}{2m}-\frac{l'^2}{2m}+\omega\right)\Big[\{b^\dagger(\vec{l'})\,\vec{p}_{\rm op}\,b(\vec{l})\}\cdot\vec{e}_\lambda(k)\,A_{\vec{k}}+$$

$$\{b(\vec{l})\,\vec{p}_{\rm op}\,b^\dagger(\vec{l'})\}\cdot\vec{e}_\lambda(k)\,A_{\vec{k}}\Big]-\frac{e^2}{4m\,(\omega\omega')^{1/2}}\sum_{\vec{l},\vec{l'},\vec{k},\vec{k'}}\delta(\vec{l}+\vec{k}-\vec{l'}-\vec{k'})$$

$$\delta\left(\frac{l^2}{2m}+\omega-\frac{l'^2}{2m}-\omega'\right)b^\dagger(\vec{l'})\,b(\vec{l})\,A^\dagger_{\vec{k'}}A_{\vec{k}}\,\vec{e}_{\lambda'}(k')\cdot\vec{e}_\lambda(k). \qquad (32)$$

Here $\vec{p}_{\rm op}$ is the momentum operator.

We are now in a position to note down additional Feynman rules for the S-matrix elements for interaction. The rules are:

(i) Draw a wavy-line for each $\vec{e}_\lambda(k)$ appearing in the interaction Hamiltonian and label it by momentum $\vec{k}$ and energy ω. The point, where this line joins a charged particle, is called a single corner and is treated as a simple vertex.

(ii) Draw two wavy-lines for each $\vec{e}_\lambda(k)\cdot\vec{e}_{\lambda'}(k')$ appearing in the interaction Hamiltonian and label them by momenta $\vec{k}$ and $\vec{k'}$ and energies ω and ω'. The point where these lines join the charged particle is called a double corner and is treated as a simple vertex.

(iii) Give a factor

$$-\frac{e}{2\mu}(\vec{p}+\vec{p'})$$

at each single corner where $\vec{p}$ and $\vec{p'}$ are the momenta of the particle line coming in and going out of the corner, respectively and μ is the mass of the particle.

(iv) Give a factor $-e^2/2\mu$ at each double corner.

(v) Conserve energies and momenta at each single corner and each double corner.

(vi) Put the factor $(2\omega)^{-1/2}$ for each external photon line which is emitted or absorbed at a single corner or double corner.

(vii) For the photon propagator appropriate to nonrelativistic case, use

$$D_{ij}(\vec{k},\omega)=-\frac{4\pi}{\omega^2-k^2}\left(\delta_{ij}-\frac{k_i\,k_j}{\omega^2}\right),\quad D_{0i}=D_{00}=0.$$

(viii) Integrate over the independent energies and momenta of internal lines.

(ix) Affix an over all factor $(-i)^n$, where n is the total number of single and double corners.

(x) Multiply the matrix element by a weight factor $W=2^g$, where $g=d-a-b$; d being the number of double corners in the diagrams; a being the number of closed photon lines (this corresponds to the situation at double corner where a photon is emitted and reabsorbed); and b being the number of pairs of double corners connected by two photon lines.

When applied to atom-photon vertex given in figures 5(a) and 5(b), these rules yield the following matrix elements.

$$M_a = \frac{e}{M(2\omega)^{1/2}} \int \frac{d^3q}{(2\pi)^3} g_f(\vec{q} + \vec{ap} + \vec{bk})(\vec{q} \cdot \vec{e}_\lambda(k)) g_i(\vec{q} + \vec{ap}), \quad (33a)$$

and

$$M_b = \frac{e}{m(2\omega)^{1/2}} \int \frac{d^3q}{(2\pi)^3} g_f(\vec{q} + \vec{bp} + \vec{ak})(\vec{q} \cdot \vec{e}_\lambda(k)) g_i(\vec{q} + \vec{bp}), \quad (33b)$$

In configuration space, these take the form

$$M_a = \frac{ie}{M(2\omega)^{1/2}} \int d^3r \{\psi_f^*(\vec{r}) \vec{\nabla} \psi_i(\vec{r})\} \cdot \vec{e}_\lambda(k) \exp(-i b \vec{k} \cdot \vec{r}), \quad (34a)$$

and

$$M_b = \frac{ie}{m(2\omega)^{1/2}} \int d^3r \{\psi_f^*(\vec{r}) \vec{\nabla} \psi_i(\vec{r})\} \cdot \vec{e}_\lambda(k) \exp(-i a \vec{k} \cdot \vec{r}), \quad (34b)$$

which are what one obtains from quantum mechanics if proper care is taken to take into account the interaction of the proton of finite mass with the photon.

From the above matrix elements it is quite evident that the contribution due to the interaction of photon with proton is small by a factor m/M compared to that with electron and is thus neglected in subsequent calculations. Here we shall consider elastic scattering of photon by hydrogen atom. The relevant Feynman diagrams are given in figures 6(a) to 6(e). The corresponding matrix elements under dipole approximation are

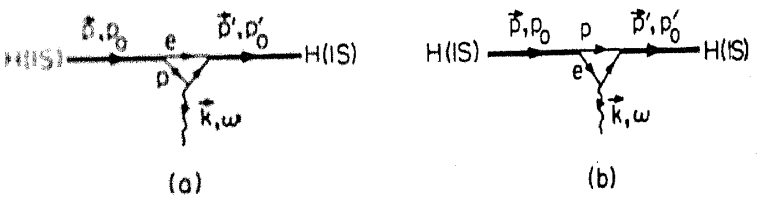
$$M_a^{fi} = \frac{e^2}{2m(\omega_i \omega_f)^{1/2}} \sum_n \frac{(\vec{e}_{\lambda'} \cdot \vec{\nabla}_{fn})(\vec{e} \cdot \vec{\nabla}_{ni})}{m(E_i - \omega_i - E_n)}, \quad (35a)$$

$$M_b^{fi} = \frac{e^2}{2m(\omega_i \omega_f)^{1/2}} \sum_n \frac{(\vec{e}_\lambda \cdot \vec{\nabla}_{fn})(\vec{e}_{\lambda'} \cdot \vec{\nabla}_{ni})}{m(E_i + \omega_f - E_n)}, \quad (35b)$$

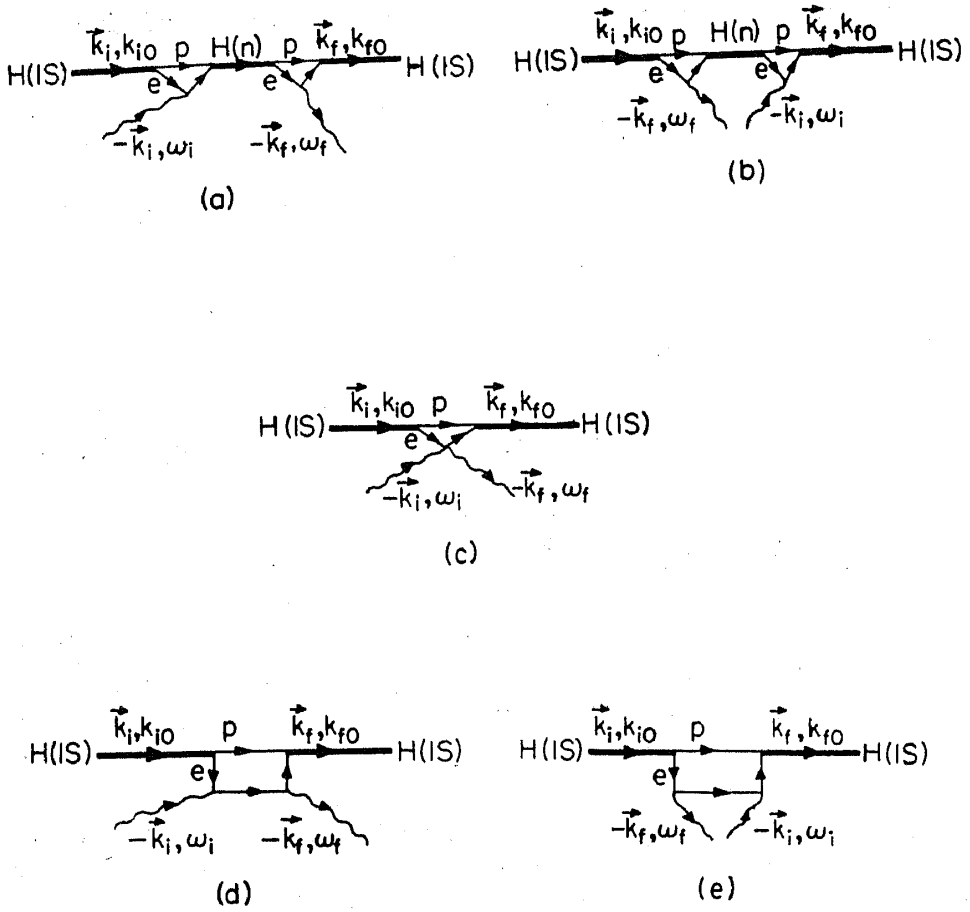
$$M_c^{fi} = \frac{e^2}{2m(\omega_i \omega_f)^{1/2}} (\vec{e}_\lambda \cdot \vec{e}_{\lambda'}) \delta_{fi}, \quad (35c)$$

$$M_d^{fi} = \frac{e^2}{2m(\omega_i \omega_f)^{1/2}} \frac{2k^2}{3\{k^2 + 2m(\epsilon_i + \omega_i)\}} (\vec{e}_\lambda \cdot \vec{e}_{\lambda'}) \delta_{fi}, \quad (35d)$$

$$M_e^{fi} = \frac{e^2}{2m(\omega_i \omega_f)^{1/2}} \frac{2k^2}{3\{k^2 + 2m(\epsilon_i - \omega_f)\}} (\vec{e}_\lambda \cdot \vec{e}_{\lambda'}) \delta_{fi}, \quad (35e)$$



Figures 5(a) and 5(b). Feynman diagrams for atom-photon vertex.



Figures 6(a) to 6(e). Feynman diagrams for photon-hydrogen atom scattering.

where n stands complete set of states of the hydrogen atom,

and $$\vec{\nabla}_n = \int d^3 r \, \psi_f^* (\vec{r}) \, \vec{\nabla} \, \psi_n (\vec{r}).$$

It will be noticed that $M_a^{fi} + M_b^{fi} + M_c^{fi} = M_{\mathrm{KH}}$ is the Kramers-Heisenberg expression for scattering of photon by an atom (Fowler 1962) and can be shown to add up to:

$$M_{\mathrm{KH}} = \frac{e^2}{2} (\omega_i \, \omega_f)^{1/2} \sum_n \left[\frac{(\vec{e}_\lambda \cdot \vec{r}_{fn}) (\vec{e}_{\lambda'} \cdot \vec{r}_{ni})}{\omega_f - E_{ni}} - \frac{(\vec{e}_{\lambda'} \cdot \vec{r}_{fn}) (\vec{e}_\lambda \cdot \vec{r}_{ni})}{\omega_i + E_{ni}} \right]. \tag{36}$$

The diagrams of figures 6(d) and 6(e) give contributions beyond the Kramers-Heisenberg formula. However, these contributions are negligible in the low frequency region; if we add the matrix elements given by equation (35d) and (35e) and take the low frequency limit, we obtain

$$\operatorname*{Lt}_{\omega \to 0} M' = \frac{\alpha^2 e^2}{6m\omega} (\omega/\epsilon_0)^2 (\vec{e}_\lambda \cdot \vec{e}_{\lambda'}), \tag{37}$$

which is small (by a factor of α^2) compared to the low frequency limit

$$\underset{\omega\to 0}{\text{Lt}}\ M_{\text{KH}} = \frac{9e^2}{16m\omega}(\omega/\epsilon_0)^2\,(\vec{e}_\lambda \cdot \vec{e}_{\lambda'}), \tag{38}$$

of the Kramers-Heisenberg matrix element (36). On the other hand, in the high frequency limit,

$$\underset{\omega\to\infty}{\text{Lt}}\ M' = \frac{8e^2k^2}{3m^3\omega}(\vec{e}_\lambda \cdot \vec{e}_{\lambda'}), \tag{39}$$

is comparable to that of the Kramers-Heisenberg matrix element, which is

$$\underset{\omega\to\infty}{\text{Lt}}\ M_{\text{KH}} = \frac{e^2}{2m\omega}(\vec{e}_\lambda \cdot \vec{e}_{\lambda'}), \tag{40}$$

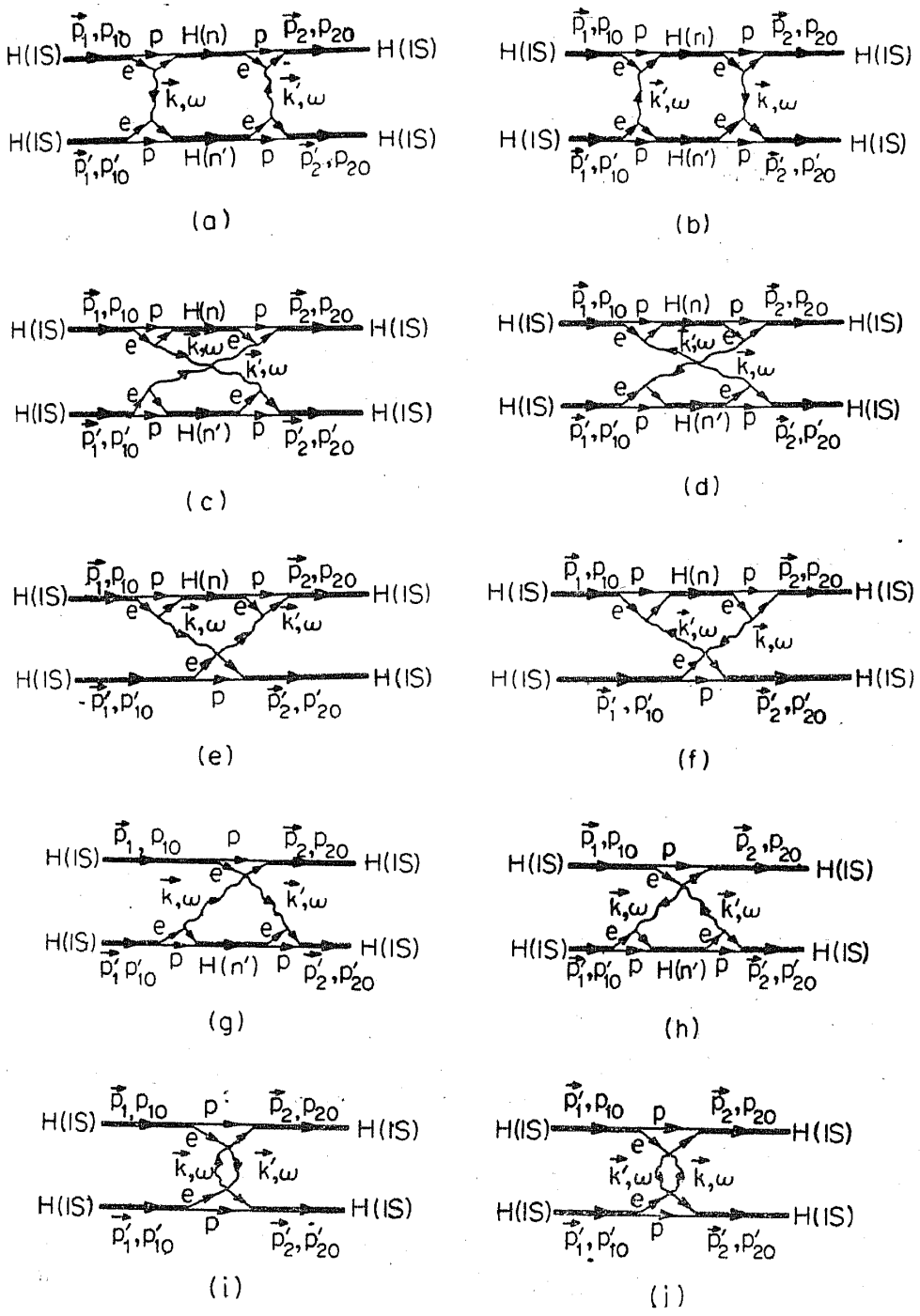
and cannot, therefore, be ignored. We thus see that our diagrammatic approach gives new results. It may be asked how such a thing comes about since our claim is that diagrammatic approach is equivalent to ordinary quantum mechanical approach. It will be noticed that the extra terms that we get arise from electron-proton intermediate state whereas in the Kramers-Heisenberg approach the intermediate states form the complete set of states of the hydrogen atom including the continuum states. It is true that these continuum states are electron-proton states, but so are the bound states. The point to note here is that both the discrete and continuum states are correleted electron-proton states and are represented by our $h(\vec{x}_1, \vec{x}_2, t)$. The proton-electron intermediate states of our diagrams (6d) and (6e) are virtual but uncorrelated proton and electron. If one were to include them in a standard quantum mechanical calculation, one would have got the extra terms that we get. Our advantage is that in a diagrammatic approach it is easier to visualise things and include all possible intermediate states.

Among other atomic processes involving photons are the Van der Waals interaction between atoms which takes place through the exchange of two photons (Feinberg and Sucher 1970). For simplicity, we consider the interaction between two hydrogen atoms for which the Feynman diagrams are given in figures 7(a) to 7(j). Use of Feynman rules and dipole approximation yields the following matrix elements.

$$M_a = ie^4 \int\int \frac{d^3k\,d\omega}{(2\pi)^4} \sum_{n,n'} \frac{E^2_{no}(r_\alpha)_{on}(r_\alpha)_{no}}{E_{no}+\omega} \cdot \frac{E^2_{n'o}(r'_{\alpha'})_{on'}(r'_{\alpha'})_{n'o}}{E_{n'o}-\omega} D_{\alpha\alpha'}(\vec{k},\omega) D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \tag{41a}$$

$$M_b = ie^4 \int\int \frac{d^3k\,d\omega}{(2\pi)^4} \sum_{n,n'} \frac{E^2_{no}(r_\alpha)_{on}(r_\alpha)_{no}}{E_{no}-\omega} \cdot \frac{E^2_{n'o}(r'_{\alpha'})_{on'}(r'_{\alpha'})_{n'o}}{E_{n'o}+\omega} D_{\alpha\alpha'}(\vec{k},\omega) D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \tag{41b}$$

$$M_c = ie^4 \int\int \frac{d^3k\,d\omega}{(2\pi)^4} \sum_{n,n'} \frac{E^2_{no}(r_\alpha)_{on}(r_\alpha)_{no}}{E_{no}+\omega} \cdot \frac{E^2_{n'o}(r'_{\alpha'})_{on'}(r'_{\alpha'})_{n'o}}{E_{n'o}+\omega} D_{\alpha\alpha'}(\vec{k},\omega) D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \tag{41c}$$



Figures 7(a) to 7(j). Feynman diagrams for Van der Waals interaction between two hydrogen atoms.

$$M_d = ie^4 \int\int \frac{d^3k\,d\omega}{(2\pi)^4} \sum_{n,n'} \frac{E^2_{no}(r_\alpha)_{on}(r_\alpha)_{no}}{E_{no}-\omega} \cdot \frac{E^2_{n'o}(r'_{\alpha'})_{on'}(r'_{\alpha'})_{n'o}}{E_{n'o}-\omega} D_{\alpha\alpha'}(\vec{k},\omega)\, D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \tag{41d}$$

$$M_e = -\frac{ie^4}{m} \int\int \frac{d^3k\,d\omega}{(2\pi)^4} \sum_{n} \frac{E^2_{no}(r_\alpha)_{on}(r_\alpha)_{no}}{E_{no}+\omega} \delta_{f'i'}\, D_{\alpha\alpha'}(\vec{k},\omega)\, D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \tag{41e}$$

$$M_f=-\frac{ie^4}{m}\int\int\frac{d^3k d\omega}{(2\pi)^4}\sum_n\frac{E^2_{no}(r_\alpha)_{on}(r_\alpha)_{no}}{E_{no}-\omega}\delta_{f'i'}\,D_{\alpha\alpha'}(\vec{k},\omega)\,D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \quad (41f)$$

$$M_g=-\frac{ie^4}{m}\int\int\frac{d^3k d\omega}{(2\pi)^4}\sum_{n'}\frac{E^2_{n'o}(r'_{\alpha'})_{on'}(r'_{\alpha'})_{n'o}}{E_{n'o}+\omega}\delta_{fi}\,D_{\alpha\alpha'}(\vec{k},\omega)\,D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \quad (41g)$$

$$M_h=-\frac{ie^4}{m}\int\int\frac{d^3k d\omega}{(2\pi)^4}\sum_{n'}\frac{E^2_{n'o}(r'_{\alpha'})_{on'}(r'_{\alpha'})_{n'o}}{E_{n'o}-\omega}\delta_{fi}\,D_{\alpha\alpha'}(\vec{k},\omega)\,D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \quad (41h)$$

$$M_i=\frac{ie^4}{2m^2}\int\int\frac{d^3k d\omega}{(2\pi)^4}\delta_{fi}\,\delta_{f'i'}\,D_{\alpha\alpha'}(\vec{k},\omega)\,D_{\alpha\alpha'}(\vec{k},+\vec{Q},\omega), \quad (41i)$$

$$M_j=\frac{ie^4}{2m^2}\int\int\frac{d^3k d\omega}{(2\pi)^4}\delta_{fi}\,\delta_{f'i'}\,D_{\alpha\alpha'}(\vec{k},\omega)\,D_{\alpha\alpha'}(\vec{k}+\vec{Q},\omega), \quad (41j)$$

where $\vec{Q}=\vec{p}'_1-\vec{p}_1=\vec{p}_2-\vec{p}'_2$ is the momentum transfer. The sum of all these matrix elements can be expressed in terms of the polarisabilities

$$\alpha(\omega)=\sum_n\left[\frac{(d_\alpha)_{on}(d_\alpha)_{no}}{E_{no}+\omega}+\frac{(d_\alpha)_{on}(d_\alpha)_{no}}{E_{no}+\omega}\right], \quad (42a)$$

$$\alpha'(\omega)=\sum_n\left[\frac{(d'_{\alpha'})_{on'}(d'_{\alpha'})_{n'o}}{E_{n'o}+\omega}+\frac{(d'_{\alpha'})_{on'}(d'_{\alpha'})_{n'o}}{E_{n'o}-\omega}\right]. \quad (42b)$$

This works out to

$$M=8\pi^2 i\int\int\frac{d^3k\,d\omega}{(2\pi)^4}\,\alpha(\omega)\,\alpha'(\omega)$$
$$\times\frac{3\omega^4-\omega^2\{k^2+(\vec{k}+\vec{Q})^2\}+\{\vec{k}\cdot(\vec{k}+\vec{Q})\}^2}{(\omega^2-k^2+i\eta)\{\omega^2-(\vec{k}+\vec{Q})^2+i\eta\}}. \quad (43)$$

The potential energy of interaction is obtained by taking the Fourier transform of this matrix-element (Berestetskii *et al* 1970):

$$V(R)=8\pi^2 i\int\int\int\frac{d^3k\,d\omega\,d^3Q}{(2\pi)^7}e^{i\vec{Q};\vec{R}}\,\alpha(\omega)\,\alpha'(\omega)$$
$$\times\frac{3\omega^4-\omega^2\{k^2+(\vec{k}+\vec{Q})^2\}+\{\vec{k}\cdot(\vec{k}+\vec{Q})\}^2}{(\omega^2-k^2+i\eta)\{\omega^2-(\vec{k}+\vec{Q})^2+i\eta\}}. \quad (44)$$

This is the interaction energy between the hydrogen atoms at the distances large compared to the atomic radius a_0. Since for a given distance, the important range

of integration for k is $k \sim R^{-1}$ and for $a_0 \ll R \ll \lambda_0$, λ_0 being the wavelength of the atomic transitions, we can neglect ω in comparison with k. The interaction energy thus obtained to be

$$V(R) = -\frac{6}{R^6} \sum_{n,\, n'} \frac{\langle n | d_z | 0 \rangle^2 \langle n' | d_z | 0 \rangle^2}{E_n + E_{n'} - 2E_0}, \tag{45}$$

which agrees with the standard result (Landau and Lifshitz 1977).

On the other hand, if the distances are such that the retardation effect comes into play, the integrations can be carried out with the limit of zero momentum transfer and static polarisability of atoms and thus the interaction energy is obtained to be

$$V(R) = -\frac{23}{4\pi} \frac{\alpha(0)\, \alpha'(0)}{R^7}, \tag{46}$$

which agrees with the result of Casimir and Polder (1948).

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