

Chapter 1

Introduction

Abstract Properties of electrons and protons, as the basic charged elements of matter, are briefly reviewed. The concept of charge and the quantum probability densities is examined and discussed under what circumstances the two are identical. Charge density and resulting properties of molecules is reviewed, together with describing adiabatic expansion for calculating their structure. Particular emphases is to derive non adiabatic coupling among the electron states of molecules.

1.1 Properties of Elementary Charges

Elementary particles of importance are the electron, proton and neutron. The electron and proton are carriers of electric charge,¹

$$e = 1.60217733 \times 10^{-19} \text{ C}$$

whilst neutron is neutral. However, in addition to charge these particles are also carriers of magnetic dipole but their values differ from one particle to the other. Their values are

$$\begin{aligned} m_e &= 9.2847701 \times 10^{-24} \text{ JT}^{-1} \\ m_p &= 1.41060761 \times 10^{-26} \text{ JT}^{-1} \\ m_n &= 9.6623707 \times 10^{-27} \text{ JT}^{-1} \end{aligned}$$

The theory predicts that neutron, based on the evidence that it has internal structure, should have a small electric dipole moment, but so far there is no strong experimental evidence for it. Therefore for any practical purpose one could assume (for the electron and proton predicted moment is even smaller) that the particles do not have this dipole moment, although from the conceptual point, and also for the consequences, yes or no is very important. However, neutron and proton might have internal distribution of charge density [20], about which there will be here more discussion.

¹SI units are used in this section.

A charge at rest produces static *electric component* of the *electromagnetic field*, the Coulomb electric field

$$\vec{E} = \frac{e}{4\pi\epsilon_0 r^2} \hat{r} \quad (1.1)$$

where $\epsilon_0 = 8.854187817 \times 10^{-12} \text{ Fm}^{-1}$ is permittivity of the vacuum, and the $\hat{r}$ indicates the unit vector. On the other hand *magnetic dipole* $\vec{m}$ at rest produces a static *magnetic component* of the electromagnetic field

$$\vec{B} = \frac{\mu_0}{4\pi r^3} [3 (\vec{m} \cdot \hat{r}) \hat{r} - \vec{m}] = -\frac{\mu_0}{4\pi} \nabla \times \left(\vec{m} \times \nabla \frac{1}{r} \right) = \nabla \times \vec{A} \quad (1.2)$$

where

$$\vec{A} = \frac{\mu_0}{4\pi} \vec{m} \times \frac{\hat{r}}{r^2}$$

and $\mu_0 = 1.2566370614 \times 10^{-6} \text{ NA}^{-2}$ is permeability of the vacuum.² The *force* that the two components of the electromagnetic field produces on another particle with charge q and magnetic dipole moment $\vec{n}$ could be written as

$$\vec{F}_{eb} = -\nabla V_{eb} \quad (1.3)$$

where the *potential energy* is

$$V_{eb} = V_c + V_d$$

The first term is the *Coulomb potential*

$$V_c = \frac{qe}{4\pi\epsilon_0 r}$$

whilst the second is the *magnetic dipole potential*

$$V_d = -\frac{\mu_0}{4\pi} \vec{n} \cdot \nabla \frac{(\vec{m} \cdot \hat{r})}{r^2}$$

The magnetic dipole potential energy is in general much smaller than the Coulomb potential energy, however, at short distances the former increases more rapidly due to its r^{-3} dependence. For the electrons one can make an estimate of the relative importance of the two forces by writing the total potential energy as

$$V_{eb} = \frac{e^2}{4\pi\epsilon_0 r} + \frac{\mu_0}{4\pi r^3} \left(\frac{e\hbar}{2M} \right)^2 \eta$$

²Magnetic induction $\vec{B}$ (Tesla) and the magnetic field $\vec{H}$ (Ampere/Meter) are related by $\mu_0 \vec{H} = \vec{B}$.

where η is of the order 1, and $\frac{e\hbar}{2M}$ is approximate magnetic dipole of the electron (Bohr magneton). The potential energy can be written in another form

$$V_{eb} = \frac{e^2}{4\pi\epsilon_0 r} \left(1 + \frac{1}{4r^2} \frac{\hbar^2}{c^2 m_e^2} \right)$$

where the relationship

$$\mu_0 \epsilon_0 = \frac{1}{c^2}$$

was used. The contribution from the magnetic dipole becomes significant when

$$\frac{1}{4r^2} \frac{\hbar^2}{c^2 m_e^2} \approx 1$$

or

$$r = \frac{\hbar}{2cm_e}$$

The Coulomb energy at this distance is

$$W_c = \frac{1}{2\pi} \frac{cm_e e^2}{\hbar \epsilon_0} \approx 7500 \text{ eV}$$

which means that in the collisions above this energy one should consider also the contribution of the magnetic dipoles of the particles to the cross sections.

Classical equations of motion that are based on the force (1.3) are not complete without equation that couples rotation of the magnetic dipole due to the *torque* that magnetic field exerts on it. The additional equation is

$$d_t \vec{m} = \gamma \vec{m} \times \vec{B}$$

where γ is a factor that relates spin to the magnetic dipole. For the three elementary particles this factor is derived from the fact that they have spin $\hbar/2$ and from the Bohr magneton one obtains

$$\begin{aligned} \gamma_{electron} &= 1.0012 \frac{e}{M_{electron}} \\ \gamma_{proton} &= 2.7928 \frac{e}{M_{proton}} \\ \gamma_{neutron} &= 1.9157 \frac{e}{M_{neutron}} \end{aligned}$$

The additional factors indicate that the Bohr magneton is only approximate value for the magnetic dipole of the elementary particles with the half spin, except for the electron for which it is given relatively accurately.

1.2 Charge Density in Molecules

Although the constituents of a molecule are protons, electrons and neutrons it is only the former two that play the essential role in the interaction with the electromagnetic field. The neutrons change the overall magnetic dipole of the nuclei and as such they are important when this type of interaction is investigated. The protons are localized in the nuclei, which, for all practical purpose, could be regarded as the point like objects with the well defined position (this statement must be taken with a caution and is only relevant for the calculation of the density of charges in molecules). The electrons, on the other hand, are delocalized over a molecule, and their position can only be satisfactory defined through the probability density

$$P(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n) = |f(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n)|^2$$

where $f(\dots)$ is the probability amplitude (wave function) for the system of n electrons. It gives the probability density of finding electron 1 at the position $\vec{r}_1$, electron 2 at $\vec{r}_2$ etc. However, the probability density of finding electron j at $\vec{r}_j$, irrespective of the whereabouts of the other electrons, is given by

$$P(\vec{r}_j) = \int |f(\vec{r}_1, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n)|^2 d^3r_1 d^3r_2 \dots d^3r_{j-1} d^3r_{j+1} \dots d^3r_n$$

which could be associated with the charge density for this electron, meaning that it could not be treated as a true charge density. Contribution of this electron to the overall Coulomb potential at $\vec{r}$ that comes from the other electrons and the nuclei is then given by

$$V_c^j = -e \int \frac{P(\vec{r}_j)}{|\vec{r} - \vec{r}_j|} d^3r_j$$

which, strictly speaking, should be interpreted as the average potential from the j -th electron. However, this expression is identical with the potential when $P(\vec{r}_j)$ is a charge density and therefore the probability density could be also associated with a charge density of the j -th electron. The difference between the true charge density and the probability density that plays the role of it is in the self repulsion term. The true charge density has a self repelling term that tends to make it unstable, whilst the probability density has no such term.

1.2.1 Self Energy of Hydrogen Atom

Hydrogen atom is a system of proton and the electron, and in the simplest approximation is that proton is at a precise position whilst the electron is delocalized. Electric potential of the proton is given by Coulomb law for a point charge, whilst that of the

electron should be calculated from the assumption that the probability density is also charge density. Therefore, the overall potential of the hydrogen atom at the distance r from the proton, for the electron in the ground state, is given by

$$V(r) = \int d^3r' \frac{P(r')}{|\vec{r} - \vec{r}'|} = \frac{\alpha^3}{2\pi^3} \int d^3r' \int d^3k \frac{e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}}{k^2 + i\eta} e^{-2\alpha r'}$$

where α is the fine structure constant, and the identity

$$\frac{1}{|\vec{r} - \vec{r}'|} = \frac{1}{2\pi^2} \int d^3k \frac{e^{i\vec{k} \cdot (\vec{r} - \vec{r}')}}{k^2 + i\eta} \quad (1.4)$$

is used. The potential is finally

$$V(r) = \frac{1}{r} - \frac{1 + \alpha r}{r} e^{-2\alpha r}$$

If the probability density is the charge density then this potential could be used to calculate self repulsion energy for the electron, and add it as the correction to the basic equation for Hydrogen atom. This energy is

$$V_{self} = \frac{\alpha}{2} \int d^3r' \int d^3r \frac{P(r)P(r')}{|\vec{r} - \vec{r}'|}$$

and by using (1.4) the final expression is

$$V_{self} = 4\alpha\pi^2 \int dr' \int dr r r' (r + r' - |r - r'|) P(r)P(r')$$

The ground state of Hydrogen atom is then solution of the radial equation

$$e g(r) = -\frac{1}{2}g''(r) - \frac{\alpha}{r}g(r) + \frac{1}{4}\alpha \int dr' dr'' \frac{(r'' + r' - |r'' - r'|)}{r'' r'} g^2(r'')g^2(r') g(r)$$

which is an integro-differential equation. One way of solving it is by iteration, where in the first step the uncorrected probability density is used to calculate the self repelling term and in the next iteration calculate new ground state probability amplitude. The iteration is repeated until the ground state eigenenergy e converges. For Hydrogen atom this eigenenergy is $e = -0.187 \alpha^2$, which should be compared with $e = -0.5 \alpha^2$ when the correction is not included. The difference is sufficient to dismiss the assumption that the probability density is the charge density. However, if another charge is placed in the field of this Hydrogen atom then its potential energy agrees very well with the observations.

1.2.2 Charge Density in Molecules

Molecules are neutral species but in most of them certain sites around atoms have slight excess of positive or negative charge. For example proton in a water molecule are slightly positively charged whilst oxygen atom is negatively charged, or Hydrogen atom in the HF molecule is slightly negatively charged whilst Fluorine is positively charged. Determining the amount of charge at the sites of a molecule is of importance in various circumstances (for example in calculating radiation by a rotating molecule Sect. 7.3.2) and therefore it is necessary to define what is meant by it. However, there is a problem with this task because positive charges are well localized in atoms whilst negative are essentially delocalized all around a molecule. The problem is well described if one asks a question what is charge density within Hydrogen atom? (here the assumption is that proton is localized at a fixed point whilst when it is not shall be discussed in Sect. 1.2.3). The answer appears simple, away from proton (nucleus) charge density is that of the probability density for the electron, which is formally correct and hence the question for a molecule seems solved. This, however, is not what is meant by charge density for a molecule, because it is defined as an effective amount of charge that a test charge experiences when approaching it. Another aspect of the concept of effective charge density is a nonuniform moving molecule, for example a rotating one. Resulting radiation comes as superposition of the individual motion of charges, nuclei and the electrons, however, it could be approximately treated by assuming that each atom is a charged particle having some effective charge. The overall charge density of a molecule is deduced from the calculation of the total potential due to all charges, and it is given by

$$V = -e \sum_{j=1}^n \int \frac{P(\vec{r}_j)}{|\vec{r} - \vec{r}_j|} d^3r_j + \sum_{i=1}^N \frac{e_i}{|\vec{r} - \vec{R}_i|}$$

where $\vec{R}_i$ is position of the i -th nuclei (e.g. with respect to the centre of mass of molecule), and the number of electrons n is equal to the number of protons, i.e. $ne = e_1 + \dots + e_N$. Because of the symmetry between electrons one has the identity

$$P(\vec{r}_j) = P(\vec{r}_k)$$

for any pair, then

$$V = -ne \int \frac{P(\vec{r}_1)}{|\vec{r} - \vec{r}_1|} d^3r_j + \sum_{i=1}^N \frac{e_i}{|\vec{r} - \vec{R}_i|} \quad (1.5)$$

and therefore the charge density in a molecule due to the electrons is

$$\rho(\vec{r}) = -neP(\vec{r}) = -ne \int |f(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n)|^2 d^3r_2 \dots d^3r_n$$

In a number of circumstance it is useful to define effective charge that one associates with an atom in a molecule, in particular atoms that are on its surface. One starts by noting that the excess of electron charge density is localized around a particular atom, and its extent is smaller than the distance of this atom to the centre of mass of a molecule. Therefore one expands potential (1.5) as

$$\begin{aligned} V &\approx -e \sum_{j=1}^n \int \frac{P(\vec{r}_j)}{r} \left(1 + \frac{\vec{r} \cdot \vec{r}_j}{r^2} \right) d^3 r_j + \sum_{i=1}^N \frac{e_i}{|\vec{r} - \vec{R}_i|} \\ &= \frac{\vec{r}}{r^3} \left[\sum_{i=1}^N e_i \vec{R}_i - ne \int P(\vec{r}_j) \vec{r}_j d^3 r_j \right] \end{aligned}$$

which has a form of potential for an electric dipole, where the dipole has the value

$$\vec{p} = \sum_{i=1}^N e_i \vec{R}_i - ne \int P(\vec{r}_j) \vec{r}_j d^3 r_j = \sum_{i=1}^N q_i \vec{R}_i$$

The parameter q_i is associated with the effective charge on atom i , and its value is calculated by the least square fit, in which case they are solutions of the set of equations

$$\sum_{i=1}^N q_i \vec{R}_k \cdot \vec{R}_i = \sum_{i=1}^N e_i \vec{R}_k \cdot \vec{R}_i - ne \int P(\vec{r}_j) \vec{R}_k \cdot \vec{r}_j d^3 r_j$$

In an external electric field, which is represented by the potential $V_{ext}(\vec{r})$, a molecule has potential energy

$$W = -ne \int \rho(\vec{r}) V_{ext}(\vec{r}) d^3 r + \sum_{i=1}^N e_i V_{ext}(\vec{R}_i)$$

In those circumstances when variation of the external field over the size of a molecule is small one can write approximately

$$V_{ext}(\vec{r}) \approx V_{ext}(\vec{R}_c) + (\vec{r} - \vec{R}_c) \cdot \nabla V_{ext}(\vec{R}_c)$$

where $\vec{R}_c$ is position of a point within the molecule, for example it is its centre of mass. The first term in the expansion, for a neutral molecule, gives

$$\begin{aligned} W_0 &= -ne \int \rho(\vec{r}) V_{ext}(\vec{R}_c) d^3 r + \sum_{i=1}^N e_i V_{ext}(\vec{R}_c) \\ &= -ne V_{ext}(\vec{R}_c) \int \rho(\vec{r}) d^3 r + V_{ext}(\vec{R}_c) \sum_{i=1}^N e_i = 0 \end{aligned}$$

where the condition

$$\int \rho(\vec{r}) d^3r = 1$$

was used.

The next term gives

$$\begin{aligned} W_1 &= -ne \int \rho(\vec{r}) (\vec{r} - \vec{R}_c) \cdot \nabla V_{ext}(\vec{R}_c) d^3r + \sum_{i=1}^N e_i (\vec{r} - \vec{R}_c) \cdot \nabla V_{ext}(\vec{R}_c) \\ &= \left[-ne \int \rho(\vec{r}) (\vec{r} - \vec{R}_c) d^3r + \sum_{i=1}^N e_i (\vec{r} - \vec{R}_c) \right] \cdot \nabla V_{ext}(\vec{R}_c) \end{aligned}$$

which can be written as

$$W_1 = \vec{d} \cdot \nabla V_{ext}(\vec{R}_c)$$

The vector $\vec{d}$ is the *permanent dipole moment* of the molecule.

There are several objections with the previous derivation: (a) variation of the external field over a molecule may not small, (b) whilst definition of a permanent dipole is well defined for small, say a diatomic, molecule, for large ones may not have meaning, and (c) definition of a permanent dipole moment assumes that the probability amplitude (wave function) for the electrons is unaffected by the external field. This is never true, but in many circumstances this effect is negligible.

1.2.3 Charge Density in Hydrogen-Like Atom

Delocalization of two oppositely charged particles, one having mass m_1 and the other mass m_2 , that are bound by a force produce charge density. The stationary bound state problem is solved in the centre of mass system, and for the relevant coordinates, which are defined as

$$\vec{r} = \vec{r}_1 - \vec{r}_2; \quad \vec{R} = \frac{m_1 \vec{r}_1 + m_2 \vec{r}_2}{m_1 + m_2}$$

the probability amplitude for the system is

$$\psi(\vec{r}, \vec{R}) = f(\vec{r}) g(\vec{R})$$

The charge density is then defined as (particle 1 has positive charge $e = 1$)

$$\begin{aligned} \rho(\vec{s}) &= \int d^3r_2 \left| f(\vec{s} - \vec{r}_2) g\left(\frac{m_1 \vec{s} + m_2 \vec{r}_2}{m_1 + m_2}\right) \right|^2 \\ &\quad - \int d^3r_1 \left| f(\vec{r}_1 - \vec{s}) g\left(\frac{m_1 \vec{r}_1 + m_2 \vec{s}}{m_1 + m_2}\right) \right|^2 \end{aligned}$$

and it is a function of the coordinates $\vec{s}$.

The coordinates are scaled with the Compton wave number $\kappa = mc/\hbar$, where m is reduced mass

$$m = \frac{m_1 m_2}{m_1 + m_2}$$

of the two particles, in which case they are dimensionless, and for a Hydrogen-like atom particle 1 is proton and particle 2 is a negatively charged particle. The ground state probability amplitude is

$$f(\vec{r}) = N e^{-\alpha r}$$

but for the probability density for the centre of mass one takes delta function³

$$|g(\vec{R})|^2 = \delta(\vec{R})$$

The last choice means that the charge density is defined for a system that is localized at the origin as a point-like particle. The radial charge density is now

$$\rho(s) = \left(1 + \frac{m_1}{m_2}\right)^3 s^2 \left| f\left[\left(1 + \frac{m_1}{m_2}\right) \vec{s}\right] \right|^2 - \left(1 + \frac{m_2}{m_1}\right)^3 s^2 \left| f\left[\left(1 + \frac{m_2}{m_1}\right) \vec{s}\right] \right|^2$$

and for the Hydrogen-like atom it is

$$\rho(s) = \frac{\alpha^3 s^2}{\pi} \left(1 + \frac{m_1}{m_2}\right)^3 e^{-2\alpha\left(1 + \frac{m_1}{m_2}\right)s} - \frac{\alpha^3 s^2}{\pi} \left(1 + \frac{m_2}{m_1}\right)^3 e^{-2\alpha\left(1 + \frac{m_2}{m_1}\right)s}$$

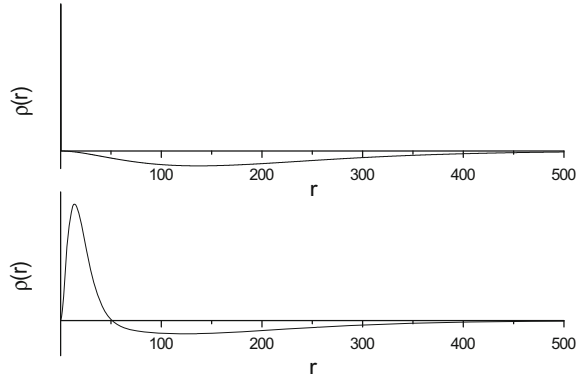
Typical charge densities are shown in Fig. 1.1 for two examples (in the appropriately scaled coordinates). If negatively charged particle is muon, which has comparable mass with the proton, the charge density has two pronounced extremes, one for the positive charge and the other for the negative (lower graph). On the other hand, if mass of negatively charged particle is that of the electron then positive charge density is concentrated in close proximity of the origin (upper graph). More realistic analysis that involves relativistic dynamics is discussed in Sect. 5.4.3.

1.2.4 Electric Dipole of Molecules

Electric dipole moment of a molecule changes when external field on a molecule is applied, and it is called induced electric dipole moment. This is manifested either as a dipole moment for molecule that has zero permanent dipole moment, or variation of the latter with the external field. The induced dipole moment is calculated from

³It should be pointed out that the delta function choice is not physical, because the size of the system as the whole cannot be smaller than the width of the binding potential. In this case this choice is only for the modelling purpose.

Fig. 1.1 Radial charge density for hydrogen atom (*upper graph*), where the positive component from proton is very close to the origin. Radial charge density for a hydrogen-like atom for muon as negatively charged particle is shown by the *lower graph*



the probability amplitude of a molecule in the presence of external field, and for a weak field one uses perturbation theory. If Hamiltonian of a molecule is H_0 and its eigenfunction is f_0 , with the eigenenergy E_0 , then in the external field the new eigenfunction f satisfies equation

$$(H_0 + V_{ext}) f = E f$$

By replacing solution with

$$f = f_0 + g$$

and likewise the eigenenergy with

$$E = E_0 + \epsilon$$

The equation for correcting term g , in the first order of perturbation, is

$$H_0 g + f_0 V_{ext} = f_0 \epsilon + g E_0$$

and by expanding it in the eigenfunctions f_j of the Hamiltonian H_0

$$g = \sum_j \varepsilon_j f_j$$

the expansion coefficients are

$$\varepsilon_m = \frac{1}{E_0 - E_m} \int f_0 V_{ext} f_m dV; \quad m \neq 0$$

Within this correction the charge density is

$$\rho(\vec{r}) = \rho_0(\vec{r}) - 2ne \int f_0(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n) g(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n) d^3r_2 \dots d^3r_n$$

where the second term is the induced dipole moment, and it is explicitly given by

$$\begin{aligned} \vec{d}_{ind} &= -2ne \int (\vec{r} - \vec{R}_c) \sum_{m \neq 0} \varepsilon_m \rho_m(\vec{r}) \\ &= -2ne \sum_{m \neq 0} \frac{\int f_0 V_{ext} f_m dV}{E_0 - E_m} \int (\vec{r} - \vec{R}_c) \rho_m(\vec{r}) d^3r \end{aligned} \quad (1.6)$$

where

$$\rho_m(\vec{r}) = \int f_0(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n) f_m(\vec{r}, \vec{r}_2, \vec{r}_3, \dots, \vec{r}_n) d^3r_2 \dots d^3r_n$$

Permanent and induced dipole moments always go together, and the magnitude of the latter is primarily determined by the differences in the eigenenergies of a molecule. In general the larger the molecule the greater the impact of the external field on the dipole moment, however, even for smaller molecules the same may hold true if the energy level spacing is small. In particular the induced dipole moment may play significant role for the time dependent external field having an impact on the spectrum a molecule.

It should be noted that the series for the induced dipole moment is not convergent, it is so called asymptotically convergent, which for the strong external fields manifests itself as the tunneling ionization.

Dipole moment for molecules is measured in the units of *debey*, and its unit value is

$$1 \text{ debey (D)} = 3.336 \times 10^{-30} \text{ Cm}$$

To understand the meaning of this unit one takes charge of the electron that is at the distance $r = 10^{-10} \text{ m}$ (typical dimension of a diatom molecule) from its opposite charge, and this dipole moment has the value

$$d = 4.8 \text{ D}$$

Atoms do not have dipole moments, they acquire it only when they are subjected to the external field. The simplest is Hydrogen atom, for which the probability amplitude of the electron, if subjected to the electromagnetic wave of the resonance frequency for $1S \rightarrow 2P$ transition, is a linear combination

$$f = \frac{a}{\sqrt{\pi a_0^3}} e^{-\frac{r}{a_0}} + \frac{b}{4\sqrt{2\pi a_0^5}} r e^{-\frac{r}{2a_0}} Y_{1,0}(\theta, \phi)$$

where $a_0 = 0.5292 \times 10^{-10}$ m is the Bohr radius. The coefficients a and b are in general complex time dependent coefficients, but without loss of generality they could be assumed real, with the property⁴

$$a^2 + b^2 = 1$$

The dipole moment is then

$$\vec{d} = -e \int d^3r f^2 \vec{r} = -e \frac{256\sqrt{2}}{243} a \sqrt{1 - a^2} a_0 \hat{z}$$

which is indeed zero if either the electron is in the ground state ($a = 1$) or the excited state ($a = 0$). Its maximal value is attained for $a = 2^{-1/2}$, when the dipole moment has the value

$$d = 1.89 \text{ D}$$

The induced dipole moment of Hydrogen atom in this electromagnetic wave therefore oscillates with this amplitude.⁵

Hydrogen atom could be permanently polarized in a constant electrostatic field. If Hydrogen atom is in the ground state, and only the $2P$ state is taken into account, then from the perturbation expression (1.6) for the dipole moment one gets

$$d = \frac{524288}{177147} \frac{e^2 a_0^4 m_e}{\hbar^2} E$$

where m_e is mass of the electron and E is the strength of the electric field. If the dipole moment should equal its amplitude when the atom is subject to the oscillating electromagnetic field then E is

$$E = \frac{729}{2048} \frac{\hbar^2}{\sqrt{2} e m_e a_0^3} = 1.29 \times 10^{11} \text{ V/m}$$

which is in practice virtually unobtainable.

Molecules, in general, may have *permanent dipole moment*, and few typical ones are given in Table 1.1 [1]. As the result molecule 1 with a dipole moment produces electrostatic field

$$\vec{E}_1 = \frac{1}{4\pi\epsilon_0 r^3} \left[3 \left(\vec{d}_1 \cdot \hat{r} \right) \hat{r} - \vec{d}_1 \right]$$

⁴Their exact time dependence is the subject of separate analysis in later discussions.

⁵It should be noted, though, that the frequency of oscillations with this amplitude is not that of the electromagnetic wave, it is a function of the strength of the field (see Rabi oscillations).

Table 1.1 Dipole moments of molecules

Molecule	d/D
CO	0.112
O ₃	0.53
H ₂ O	1.85
CN ₂ H ₂	4.27
KBr	10.41

and another molecule with a dipole $\vec{d}_2$ in this field has potential energy

$$V_{dip-dip} = -\frac{1}{4\pi\epsilon_0 r^3} \left[3 (\vec{d}_2 \cdot \hat{r}) (\vec{d}_1 \cdot \hat{r}) - \vec{d}_1 \cdot \vec{d}_2 \right]$$

where r is separation between the dipoles and $\hat{r}$ points from one to the other molecule. Potential energy depends on the relative orientation of the two dipoles: the interaction could be attractive (parallel configuration) or repulsive (antiparallel configuration). This feature of interaction between the two dipoles results in the *torque* that the field of one molecule exerts on the other, which has the form

$$I_2 d_t \vec{\omega}_2 = \vec{d}_2 \times \vec{E}_1$$

where I_2 is momentum of inertia and $\vec{\omega}_2$ is the angular velocity of the molecule 2 (for the equation of the molecule 1 the indices are interchanged) given by (the index is omitted)

$$\vec{\omega} = -d_t \theta \sin \phi \hat{x} + d_t \theta \cos \phi \hat{y} + d_t \phi \hat{z}$$

In terms of the spherical angles the dipole $\vec{d}$ is

$$\vec{d} = d (\sin \theta \cos \phi \hat{x} + \sin \theta \sin \phi \hat{y} + \cos \theta \hat{z})$$

Dipole-dipole interaction is dominant when the molecules are separated, and its absolute magnitude is better expressed in the scaled units, being

$$V_{dip-dip} = -\frac{0.6242}{r^3} \left[3 (\vec{d}' \cdot \hat{r}) (\vec{d} \cdot \hat{r}) - \vec{d} \cdot \vec{d}' \right]$$

where the separation between them is now measured in the units of 10^{-10} m (Angstroms) and the dipole moments are given in debyes. Depending on the molecules but in general dipole-dipole interaction dominates until the distances of the order 10 Å. A simpler system is atom-molecule system the potential is

$$V_{dip-atom} = -\frac{2.998q}{r^2} \vec{d} \cdot \hat{r}$$

where the charge of atom q is in the units of elementary charge. On the other hand if atom is neutral then the dipole field induces charge separation in it, which is of the order r^{-2} , and the interaction decays more rapidly, as $V_{dip-atom} \sim r^{-4}$.

1.2.5 Van der Waals Potential

Neutral atoms or molecules, without polarization of charge density still exerts a force on another species with the same characteristics. The force is responsible for formation of clusters, which is manifested, for example, as formation of liquids from gas phase, adhesion and it is essentially the explanation of the Casimir effect [2]. The theory that explains the force is very well documented [2,3] and here we give a brief overview of its essentials.

Relatively few molecules do not have electric dipole moment, but atoms and the molecules without it exert a force on the like species by attractive force that arises from the finite extent of the charge density of the electrons. The force is expected to be weak but significant at large separations of the species, where the chemical forces are negligible. Therefore at these separations the electron densities of these species do not overlap appreciable, the assumption that will be used in the following analysis. For simplicity this force is derived for two Hydrogen atoms, the derivation that has straightforward generalization to more complex situations.

Based on the assumption that the two Hydrogen atoms are well separated the potential energy of the system is

$$V_W = \frac{q^2}{r} - \frac{q^2}{|\vec{r} + \vec{r}_2|} - \frac{q^2}{|\vec{r} - \vec{r}_1|} + \frac{q^2}{|\vec{r} + \vec{r}_2 - \vec{r}_1|}$$

$$\approx q^2 \left[\frac{\vec{r}_2 \cdot \vec{r}_1}{r^3} - 3 \frac{(\vec{r} \cdot \vec{r}_2)(\vec{r} \cdot \vec{r}_1)}{r^5} \right]$$

where $\vec{r}$ is separation of atom 2 from atom 1, which is placed at the origin. The vectors $\vec{r}_2$ and $\vec{r}_1$ are positions of the the electrons 2 and 1 relative to their respective nuclei. In the last step expansion is made in the ratio of r_n/r , and the leading term retained. This interaction perturbs electronic states, and the (nearly) complete set of the unperturbed ones are (the continuum states are not included)

$$F_{n_1, n_2}^{(0)}(\vec{r}_1, \vec{r}_2) = f_{n_1}^{(0)}(\vec{r}_1) f_{n_2}^{(0)}(\vec{r}_2) \quad (1.7)$$

where the assumption of the non overlapping electronic probability amplitudes was implemented. Impact of interaction potential V_W on the state (n_1, n_2) is calculated from the perturbation expansion, and the probability amplitude with the leading correction is⁶

⁶The convenient $\langle || \rangle$ abbreviates integral over all variables that are involved.

$$F_{n_1, n_2}^{(1)} = F_{n_1, n_2}^{(0)} + \sum_{m_1, m_2} \frac{\langle F_{n_1, n_2}^{(0)} | V_W | F_{m_1, m_2}^{(0)} \rangle}{E_{n_1, n_2}^{(0)} - E_{m_1, m_2}^{(0)}} F_{m_1, m_2}^{(0)}$$

Correction to the unperturbed eigenenergies is then

$$\begin{aligned} & \left\langle F_{n_1, n_2}^{(0)} | V_W | \sum_{m_1, m_2} a_{n_1, n_2; m_1, m_2} F_{m_1, m_2}^{(0)} \right\rangle \\ &= \langle F_{n_1, n_2}^{(0)} | V_W | F_{n_1, n_2}^{(0)} \rangle + \sum_{m_1, m_2} \frac{|\langle F_{n_1, n_2}^{(0)} | V_W | F_{m_1, m_2}^{(0)} \rangle|^2}{E_{n_1, n_2}^{(0)} - E_{m_1, m_2}^{(0)}} \end{aligned} \quad (1.8)$$

which is r dependent and is associated with the long range atom-atom interaction, known as the Van der Waals potential.

Potential V_W represents essentially electric dipole-dipole interaction, which means that induces also correlation between the two of them. This correlation effect is calculated from

$$\langle \hat{r}_1 \cdot \hat{r}_2 \rangle = \int d^3r_1 d^3r_2 F_{n_1, n_2}^* (\hat{r}_1 \cdot \hat{r}_2) F_{n_1, n_2} \quad (1.9)$$

and by using approximation for the probability amplitude

$$\langle \hat{r}_1 \cdot \hat{r}_2 \rangle \approx 2 \operatorname{Re} \left[\sum_{m_1, m_2} \frac{\langle F_{n_1, n_2}^{(0)} | V_W | F_{m_1, m_2}^{(0)} \rangle}{E_{n_1, n_2}^{(0)} - E_{m_1, m_2}^{(0)}} \langle F_{n_1, n_2}^{(0)*} | \hat{r}_1 \cdot \hat{r}_2 | F_{m_1, m_2}^{(0)} \rangle \right]$$

Previous derivation is valid under the assumption of no degeneracy, meaning that no two pair of energies $E_{n_1, n_2}^{(0)}$ and $E_{m_1, m_2}^{(0)}$ are equal for any set of quantum numbers unless $(n_1, n_2) = (m_1, m_2)$. The problem arises because for Hydrogen atom, as an example, the probability amplitude is specified by three quantum numbers (n, l, m) whilst the appropriate eigenenergy is a function of only the principal quantum number n and independent of the angular momentum ones l and m . Therefore for the quantum number n the eigenenergies are n^2 degenerate. Degeneracy also arises when two atoms are identical, in which case by interchanging the pair (n_1, n_2) with (n_2, n_1) the eigenenergies are the same. Previous analysis that is based on the non-degenerate perturbation expansion must therefore be replaced by the theory that takes into account degeneracy.

In the degenerate perturbation expansion one isolates a set of degenerate states, say there are d degenerate ones. If f_n are eigenstates of unperturbed Hamiltonian then the first d states (for convenience the set of eigenstates are ordered in this way) have the same eigenenergy e_d . One defines a new basis set h_n , which is a linear combination of f_n but only for the indices smaller or equal to d whilst the rest are unaltered. The first d states are g_n for $n \leq d$ are defined so that they diagonalize perturbing potential V_W , i.e.

$$(\tilde{U})_{n,i} \langle f_i | V_W | f_j \rangle U_{j,m} = \langle h_n | V_W | h_m \rangle = e_n^{(1)} \delta_{n,m} \quad (1.10)$$

which means that

$$h_m = f_j U_{j,m}$$

In the new basis set one uses the rules of the non-degenerate perturbation theory, thus the first order corrected eigenenergies, for all n , are

$$e_n^{(1)} = e_n + \langle h_n | V_W | h_n \rangle$$

and the first order corrected probability amplitudes are

$$h_n^{(1)} = h_n + \sum_m \frac{\langle h_n | V_W | h_m \rangle}{e_n - e_m} h_m$$

The second order corrected eigenenergies are therefore

$$e_n^{(2)} = e_n + \langle h_n | V_W | h_n^{(1)} \rangle = e_n + \langle h_n | V_W | h_n \rangle + \sum_m \frac{|\langle h_n | V_W | h_m \rangle|^2}{e_n - e_m} \quad (1.11)$$

Degenerate perturbation expansion is the most demanding when two atoms are identical. The two indices that specify the state of each atom (each index should be understood as a set of quantum numbers, 3 in the case of Hydrogen atom) do not only individually represent degenerate states but also upon the exchange of them one gets also another set that is degenerate with the previous one. For example, if one seeks Van der Waals potential between two Hydrogen atoms where one is in $n = 1$ state and the other in $n = 2, l = 1$ and $m = 0$ state one cannot but not to include the other l and m states in this atom. In general one combination has 4 states and upon interchange of the states there are another 4 states. There are, therefore, altogether 8 states are degenerate and should be considered for calculating the potential. However, within these states some are not coupled by the matrix element in (1.10) and their eigenenergies are not affected by transformation, but their probability amplitudes are. Furthermore, the diagonal elements in this coupling matrix are zero therefore the sum of the eigenvalues in (1.10) are zero. This means that for this system the states whose eigenenergies are affected by the transformation come in pairs, one for which the shift from their unperturbed values is positive and the other that is negative. Upon the exchange of atoms the two affected states are of the opposite sign, being result of the symmetry of V_W with respect to this exchange.

Correlation of the two electric dipoles (1.9), in the case of degeneracy is approximately

$$\langle \hat{r}_1 \cdot \hat{r}_2 \rangle_n \approx \langle h_n | \hat{r}_1 \cdot \hat{r}_2 | h_n \rangle \quad (1.12)$$

and it is not in general zero.

In the previous analysis the states for which the Van der Waals potential was defined are fixed, however, in most applications regarding dynamics of atoms one works with a general expansion

$$G = \sum_{m_1, m_2} c_{m_1, m_2} F_{m_1, m_2}^{(0)}$$

where the coefficients are, in general, time dependent, therefore the Van der Waals force is also time dependent. Straightforward generalization of the previous. non degenerate, perturbation analysis gives for the Van der Waals potential

$$\begin{aligned} & \langle G | V_W | G^{(1)} \rangle \\ &= \sum_{m_1, m_2} \sum_{n_1, n_2} c_{m_1, m_2}^* c_{n_1, n_2} \left[\frac{\langle F_{m_1, m_2}^{(0)} | V_W | F_{n_1, n_2}^{(0)} \rangle +}{\sum_{i_1, i_2} \frac{\langle F_{n_1, n_2}^{(0)} | V_W | F_{i_1, i_2}^{(0)} \rangle}{E_{n_1, n_2}^{(0)} - E_{i_1, i_2}^{(0)}} \langle F_{m_1, m_2}^{(0)} | V_W | F_{i_1, i_2}^{(0)} \rangle} \right] \end{aligned}$$

In the case of degeneracy one defines a new basis set based on the recipe that was given earlier. The degenerate states form a subset of the complete set, and for each one of them one performs transformation that was described earlier. After the transformation the unitary matrix that transforms the entire basis set is a block matrix, where each one transforms a particular degenerate subset. This unitary matrix is used to define a new basis set which used in the perturbation expansion.

1.2.5.1 Two Hydrogen Atoms

Two Hydrogen atoms is the simplest system where to describe calculation of the Van der Waals potential, and if both of them are in their ground state there is no degeneracy and it is calculated from (1.8). The ground state probability amplitude is $F[1, 0, 0; 1, 0, 0]$ (the indices n , l and m are written in the brackets for better visualization, where r_1 is associated with the first set whilst r_2 with the second) and in the simplest approximation it is in general coupled to $F[2, l, m; 1, 0, 0]$, $F[1, 0, 0; 2, l, m]$ and $F[2, l, m; 2, l, m]$. However, by the symmetry considerations it is only coupled to $F[2, 1, -1; 2, 1, 1]$, $F[2, 1, 1; 2, 1, -1]$ and $F[2, 1, 0; 2, 1, 0]$ in which case one gets for the Van der Waals potential⁷

$$V_W \approx -\frac{2.46 q^2}{\alpha^6 r^6}$$

where q is electric charge and α is fine structure constant (appropriate units are used).

One is tempted to assume that the same reasoning applies for the potential when both atoms are in $2S$ state. Although this state is degenerate with $2P$ states that would not be a problem if the coupling between them is zero. However, this is not the case

⁷In the calculations it is assumed that the two atoms are along the z axes.

because $F[2, 0, 0; 2, 0, 0]$ is coupled to $F[2, 1, -1; 2, 1, 1]$, $F[2, 1, 1; 2, 1, -1]$ and $F[2, 1, 0; 2, 1, 0]$, and therefore one must use degenerate perturbation expansion. The complete set of degenerate probability amplitudes for $n = 2$ when both atoms are included has 16 terms, and out of 136 coupling terms only 12 are coupled. The list of those coupled states is in (1.14), but there are 8 states that are not coupled to any other. In practice one forms the coupling matrix (1.10) with the entire set, and combination of basis set functions that have zero eigenvalue correspond to the uncoupled set. 8 eigenvalues that are not zero are $\{\pm 22.05, \pm 18, \pm 9, \pm 9\}$. Therefore Van der Waals potential between two atoms in $2S$ state has no meaning because these states come in a linear combination with the states from $2P$. However, among the linear combinations those with the largest absolute eigenvalue have the largest weight and the two are given by

$$F_{2S} = \frac{1}{\sqrt{2}} F[2, 0, 0; 2, 0, 0] \mp \frac{1}{\sqrt{3}} F[2, 1, 0; 2, 1, 0] \mp \frac{1}{\sqrt{12}} F[2, 1, 1; 2, 1, -1] \mp \frac{1}{\sqrt{12}} F[2, 1, -1; 2, 1, 1] \quad (1.13)$$

which are symmetric with respect to the interchange of two atoms. For each of the two linear combinations one associates a potential, one is attractive, corresponding to the negative eigenenergy, and the other is repulsive, corresponding to the positive one. Important feature of these potentials is their rate of decay is r^{-3} , which is much slower than r^{-6} for a typical Van der Waals interaction. The two potentials have also different sign, one describes attraction of the two atoms and the describe repulsion. The states (1.13) describe interaction of two atoms in predominantly $2S$ states and to show this one calculates correlation (1.12), which is shown to be zero. The result supports this conjecture because correlation is zero if the two atoms are in a spherically symmetric states.

$\langle 2, 0, 0; 2, 0, 0 2, 1, -1; 2, 1, 1 \rangle$	$\langle 2, 0, 0; 2, 0, 0 2, 1, 0; 2, 1, 0 \rangle$
$\langle 2, 0, 0; 2, 0, 0 2, 1, 1; 2, 1, -1 \rangle$	$\langle 2, 0, 0; 2, 1, -1 2, 1, -1; 2, 0, 0 \rangle$
$\langle 2, 0, 0; 2, 1, 0 2, 1, 0; 2, 0, 0 \rangle$	$\langle 2, 0, 0; 2, 1, 1 2, 1, 1; 2, 0, 0 \rangle$
$\langle 2, 1, -1; 2, 0, 0 2, 0, 0; 2, 1, -1 \rangle$	$\langle 2, 1, -1; 2, 1, 1 2, 0, 0; 2, 0, 0 \rangle$
$\langle 2, 1, 0; 2, 0, 0 2, 0, 0; 2, 1, 0 \rangle$	$\langle 2, 1, 0; 2, 1, 0 2, 0, 0; 2, 0, 0 \rangle$
$\langle 2, 1, 1; 2, 0, 0 2, 0, 0; 2, 1, 1 \rangle$	$\langle 2, 1, 1; 2, 1, -1 2, 0, 0; 2, 0, 0 \rangle$

(1.14)

The other linear combinations involve states $2S$ and $2P$, for example the two that correspond to the second largest in magnitude eigenenergies are

$$F_{2S} = \frac{1}{\sqrt{2}} F[2, 1, 0; 2, 0, 0] \mp \frac{1}{\sqrt{2}} F[2, 0, 0; 2, 1, 0]$$

and they produce the Van der Waals potential when the P state has quantum numbers $l = 1$ and $m = 0$. One state is antisymmetric with respect to the interchange of atoms and the potential is repulsive. The other is symmetric and the potential is attractive. Correlation (1.12) is not zero, and in the former case it is $\langle \hat{r}_1 \cdot \hat{r}_2 \rangle = -1/4$, thus indicating that on average the two dipoles are antiparallel, which means repulsion.⁸ For the symmetric state the correlation is $\langle \hat{r}_1 \cdot \hat{r}_2 \rangle = 1/4$, and represents attraction. The other two linear combinations represent similar interactions.

1.3 Structure of Molecules

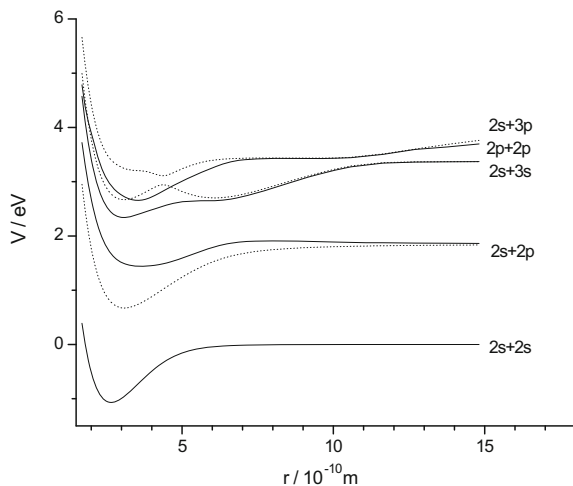
Constituents of molecules are electrons and nuclei, but when it comes to determining their structure and dynamics the two sets of particles play different role. The key parameter that distinguishes them is their mass, the nuclei having much larger than the electrons. However, this statement should be taken with some caution, depending on how it is applied. The intuition tells that if the nuclei of a mass M and the electrons of the mass m have nearly equal energy E then the ratio of their velocities is proportional to $\sqrt{m/M}$. This means that nuclei move more slowly than the electrons, for example kinetic energy of the protons in the ground state of Hydrogen molecule is of the order 0.1 eV whilst that of the electrons is 10 eV and so the ratio of the two velocities is $v_{prot}/v_{elec} \approx \sqrt{0.1/10 \times 1/2000} \approx 10^{-3}$. Furthermore the momentum exchange between the electrons and the nuclei is small, again due to the ratio of their masses, and based on the two arguments one assumes a similar concept as in thermodynamics, the adiabatic approximation. The approximation applies to a system with two groups of degrees of freedom⁹ where each one has independent dynamics of the other. In the case of molecules, therefore, the adiabaticity, the Born-Oppenheimer approximation as it is also called, means that the motion of nuclei is independent of the motion of the electrons. Validity of the Born-Oppenheimer approximation has been discussed on various occasions [5–8], whilst here in Sect. 1.3.2 its limitations are discussed more explicitly on example of Hydrogen atom in harmonic oscillator.

In practice the adiabatic approximation is formally implemented in the following way. For a fixed configuration of nuclei one calculates eigenstates of the electrons, and the relevant probability amplitudes are $f_n(r, R)$, where n refers to a set of indices that characterize a particular electronic state. r is the set of coordinates for the electrons, in the form $r = \{x_1, y_1, z_1, x_2, y_2, \dots\}$ whilst R is similar set for the nuclei. Energy of the electronic states depend parametrically on the coordinates R and it is written as $e_n(R)$, meaning that if E is the overall energy of molecule then energy of the nuclei is $E - e_n(R)$. In equation for the nuclei, therefore, the energy $e_n(R)$ plays

⁸It should be noted that the two dipoles are defined with respect to the line that connects two atoms, thus antiparallel means electron-proton-proton-electron configuration.

⁹In thermodynamics the parameters that determine a system are pressure, volume, temperature and the heat bath with which the system has energy exchange. The adiabatic approximation means that the temperature always changes in unison with that of the heat bath and it is not affected by the changes in pressure and volume.

Fig. 1.2 Electronic energies of Li_2 molecule [4] as a function of their internuclear separation. The energies are labeled by the dissociation states of the molecule



the role of potential in which they move due to, roughly speaking, averaging over the electronic degrees of freedom. Typical potentials for $Li-Li$ molecule are shown in Fig. 1.2, which are characterized by the asymptotic states of individual atoms when they are pulled apart. Although the procedure is straightforward the question is when one expects the adiabatic approximation to fail?

The answer to this question will be given on a general level but a simpler one derives from an order of magnitude argument. The adiabatic approximation is valid provided the electrons move much faster than nuclei, and so its failure is expected when the two velocities are nearly equal. This, however, means that kinetic energy of the nuclei should be greater than the same for the electrons by the ratio of the mass of the former to the mass of the latter. This ratio is typically of the order 10^4 and so if binding energy of the electrons (valence electrons) is of the order 1 eV then energy of the nuclei should be roughly 10^4 eV, which is indeed very large. However, there may be circumstances when the adiabatic approximation fails for much smaller kinetic energy of the nuclei, e.g. when atoms are in highly excited states (Rydberg states) and their binding energy is much smaller. For example, the electron in Hydrogen atom in the state with the principal quantum number $n = 100$ has energy of the order 10^{-3} eV and so it is expected that adiabatic approximation would fail when nuclei have few eV.

The essence of breakdown of the adiabatic approximation could be demonstrated on a simple classical model. In this model the electron is coupled to the motion of the nucleus whilst the latter is coupled to an external potential. The simplest is to assume Hydrogen atom on which the force $\vec{F}(\vec{R})$ is applied and analyze how the motion of the electron is affected by it. Adiabatic approximation assumes that motion of the electron is independent of motion of the proton, or to be more precise, energy of the electron is affected but its change is smaller than some predetermined value. There are two sets of classical equations that describe this system. One for the proton, and

if it has the mass M and the position vector $\vec{R}$ it is given by

$$M \ddot{\vec{R}} = \vec{F}(\vec{R}) + \vec{G}(\vec{R} - \vec{r})$$

On the other hand, equation for the electron is

$$m \ddot{\vec{r}} = -\vec{G}(\vec{R} - \vec{r})$$

where $\vec{G}(\vec{R} - \vec{r})$ is force between the electron and proton, the Coulomb force

$$\vec{G}(\vec{R} - \vec{r}) = -\nabla V_{Coul}(|\vec{R} - \vec{r}|) = -\frac{e^2}{4\pi\epsilon_0} \frac{\vec{R} - \vec{r}}{|\vec{R} - \vec{r}|^3}$$

By defining

$$\vec{u} = \vec{R} - \vec{r}$$

then equation for the electron is

$$m \ddot{\vec{u}} = \vec{G}(\vec{u}) + \frac{m}{M} \vec{F}(\vec{R}) + \frac{m}{M} \vec{G}(\vec{u})$$

The adiabatic approximation is to neglect the last two terms, which are of the order mM^{-1} , when trajectory for the electron is

$$\vec{r} = \vec{R} - \vec{u}(t)$$

which depends parametrically on the coordinates of proton. By definition this is adiabatic solution for the electron. Motion of the proton is then derived from equation

$$M \ddot{\vec{R}} = \vec{F}(\vec{R}) + \vec{G}(\vec{u})$$

where $\vec{u}$ is solution of adiabatic equation for the electron. Measure of this approximation is energy of proton, whose change in time is given by

$$\Delta E_{pr} = \int dt \dot{\vec{R}} \cdot \vec{G}[\vec{u}(t)]$$

and motion is adiabatic if ΔE_{pr} is smaller than some predetermined value.

1.3.1 Adiabatic Approximation

Deriving rigorous adiabatic approximation for the system of N_{el} electrons and N_{nu} nuclei one starts from equation

$$[T_{el}(r) + T_{nu}(R) + V(r, R)] f(r, R) = E f(r, R) \quad (1.15)$$

where $T_{el}(r)$ is kinetic energy operator for the electrons, $T_{nu}(R)$ is the same for the nuclei and $V(r, R)$ is the potential energy of the whole system. Few words about the coordinates and the symbolic way how they are represented. The symbol r represents the Cartesian coordinates set $r = \{x_1, y_1, z_1, x_2, y_2, \dots\}$ of the individual electrons whilst R stands for the set of nuclear coordinates in the centre of mass coordinates system, which is obtained by neglecting the mass of the electrons. Therefore the components $R = \{X_1, Y_1, Z_1, X_2, Y_2, \dots\}$ are obtained from the coordinates of individual nuclei by removing the centre of mass coordinate and the remaining are chosen so that the kinetic energy operator is in the form

$$T_{nu}(R) = -\frac{\hbar^2}{2} \sum_n^{3N_{nu}-3} M_n^{-1} \Delta_{R_n} = -\frac{\hbar^2}{2} M^{-1/2} \nabla \cdot M^{-1/2} \nabla \equiv T_{nu}^{1/2}(R) T_{nu}^{1/2}(R) \quad (1.16)$$

where M is a $3N_{nu} - 3$ (the centre of mass coordinates are removed) diagonal matrix of the masses that are related to those of the nuclei (see Appendix D), which on the diagonal has the values $M_{j,j} = \{M_1, M_1, M_1, M_2, M_2, \dots\}$. The operator ∇ is a single column matrix having the elements

$$\nabla = \{\nabla_{X_1}, \nabla_{Y_1}, \nabla_{Z_1}, \nabla_{X_2}, \nabla_{Y_2}, \dots\}.$$

In contrast to the nuclear kinetic energy the operator $T_{el}(r)$ is the sum of contributions from individual electrons. The parameter E is the total energy of the system.

Overall motion of a molecule appears as a nonessential information and could be removed from the solution of equation (1.15). The removal is indeed justified in many circumstances but there are processes when it is important to know motion of the centre of mass of a molecule. For example, when the electromagnetic field interacts with a molecule then the result is also its translational motion, which means that there is coupling between all the coordinates involved. In this case it is imperative to including the centre of mass coordinates into the dynamics equations. These processes are not analyzed here, in Chap. 6 they are analyzed in details for atoms, the interest is focused on investigating how to implement the adiabatic approximation for an isolated molecule and under what circumstances it is applicable.

Adiabatic, or Born-Oppenheimer, approximation is briefly or in more details reviewed in almost any textbook where molecular structure is analyzed. Nowadays the methods of calculating molecular structures has grown to be a very sophisticated tool, but always in the background is this approximation. However, the problem still

remains corrections to this approximation, the non adiabatic processes, which is the emphases in this section.

The adiabatic approximation is derived by writing solution of equation (1.15) in the form of expansion

$$f(r, R) = \sum_n g_n(r, R) w_n(R) \quad (1.17)$$

where $g_n(r, R)$ are eigenfunctions of the electronic Hamiltonian for a fixed configuration of a molecule, i.e.

$$H_{el}(r, R) g_n(r, R) = W_n(R) g_n(r, R)$$

However, here another approach is adopted that will prove to be useful in later analysis. One starts by the diabatic expansion, which essentially means that for a fixed configuration of nuclei R_0 one defines a complete set of eigenfunctions of the electronic Hamiltonian (for simplicity it is assumed that all electronic states are bound.) by solving equation

$$[T_{el}(r) + V(r, R_0)] g_n(r) = W_n(R_0) g_n(r) \quad (1.18)$$

For any other nuclear configuration one then writes expansion for the solution of equation (1.15) as

$$f(r, R) = \sum_n g_n(r) w_n(R)$$

This expansion is expected to be poorly convergent for all R but in a small vicinity of R_0 it may have advantages over the adiabatic expansion. By replacing expansion in (1.15) one gets a set of equations for the “coefficients” $w_n(R)$, which are in a matrix form given by

$$T_{nu}(R) w(R) = [E - O^{di}(R)] w(R) \quad (1.19)$$

where $O^{di}(R)$ is a matrix with the elements

$$\begin{aligned} O_{i,j}^{di}(R) &= \int d^{3N_d} r [V(r, R) - V(r, R_0)] g_i(r) g_j(r) + W_i(R_0) \delta_{i,j} \\ &\equiv \langle g(r) | O(r, R) | g(r) \rangle_{i,j} \\ &= \langle i | V(r, R) - V(r, R_0) | j \rangle^{di} + W_i(R_0) \delta_{i,j} \end{aligned} \quad (1.20)$$

where the superscript indicates the diabatic basis. One now defines a unitary matrix U that diagonalizes O^{di} , i.e.

$$\tilde{U}(R) O^{di}(R) U(R) = \lambda(R) \equiv O^{ad}(R) \quad (1.21)$$

where $\lambda(R)$ is a diagonal matrix. The role of the matrix U is deduced from this property, it changes the basis set of the electronic functions, from those fixed at R_0 to those at R . Explicitly

$$\tilde{U}(R)g(r) = g(r, R) \quad (1.22)$$

which is changing from diabatic basis set in expansion (1.19) into the adiabatic in expansion (1.17). Therefore, study of the matrix $U(R)$ is bridging the gap between the two expansions.

The diabatic set of equations (1.19) is transformed by using the relationship (1.22), when one gets

$$T_{nu}(R)w(R) = [E - U(R)O^{ad}(R)\tilde{U}(R)]w(R)$$

where now the matrix elements are in the adiabatic basis. In accordance with the transformation of the electronic basis functions the nuclear ones must also be modified by writing

$$W(R) = \tilde{U}(R)w(R)$$

and so they satisfy the set of equations

$$\tilde{U}(R)T_{nu}(R)[U(R)W(R)] = [E - O^{ad}(R)]W(R) = [E - \lambda(R)]W(R)$$

By using nuclear kinetic energy operator (1.16) the left side is transformed, where one has to calculate derivatives $\nabla_{R_n}U(R) \equiv U'_n(R)$. By making parametrization

$$U'_n(R) = U(R)\eta_n(R)$$

and from the definition of the matrix $U(R)$ it is deduced

$$\eta_{n;i,j}(R) = \begin{cases} \frac{\langle i | V'_n(r, R) | j \rangle^{ad}}{\lambda_j(R) - \lambda_i(R)} ; & i \neq j \\ 0 & ; \quad i = j \end{cases} \quad (1.23)$$

where the superscript indicates the adiabatic electronic basis. Further derivatives are similarly deduced, and given by

$$\begin{aligned} \nabla_{R_n}\eta_{i,j}(R) &= \frac{\langle i | V''_n(r, R) | j \rangle^{ad}}{\lambda_j(R) - \lambda_i(R)} \\ &+ \frac{2\lambda_k(R) - \lambda_i(R) - \lambda_j(R)}{\lambda_j(R) - \lambda_i(R)}\eta_{n;i,k}(R)\eta_{n;k,j}(R) - \frac{\lambda'_{n;j}(R) - \lambda'_{n;i}(R)}{\lambda_j(R) - \lambda_i(R)}\eta_{n;i,j}(R) \end{aligned}$$

and

$$\lambda'_{n;i}(R) = \langle i | V'_n(r, R) | i \rangle^{ad}$$

so that the final set of equations is

$$-\frac{\hbar^2}{2} \sum_n^{3N_{nu}-3} M_n^{-1} [\nabla_{R_n} + \eta_n(R)]^2 W(R) = [E - \lambda(R)] W(R) \quad (1.24)$$

where one distinguishes two terms of different order in powers of mass M . The term $\nabla_{R_n} W(R)$ is of the order $M^{1/2}$ whilst the matrix η is independent of mass and therefore by the criterion that the nuclear mass is large one neglects this term and the set simplifies

$$T_{nu}(R) W(R) = [E - \lambda(R)] W(R)$$

which is the adiabatic approximation, or the Born-Oppenheimer approximation.

In general η is small and the mass of the nuclei is large which means that the adiabatic approximation is quite accurate. However, the matrix elements of η depend on the separation between the eigenvalues $\lambda_i(R)$, as shown in their definition (1.23), and their proximity is a measure of the failure of the adiabatic approximation. In order to understand that better it is worth investigating the source of encounter of the electronic energies $\lambda(R)$, and for that one should recall how in practice they are calculated. Direct solution of equations (1.18) is not feasible, instead one resorts to the variational principle, and the simplest of the methods is the Hartree-Fock.¹⁰ It essentially assumes a fixed electronic configuration, being a product (properly antisymmetrized though) of functions that describe independent electronic states, and then the parameters in these functions are optimized to minimize the lowest eigenvalue of the integral

$$W(R_0) = \min \left\{ \int d^{3N_{el}} r g_{tr}(r) [T_{el}(r) + V(r, R_0)] g_{tr}(r) \right\} \quad (1.25)$$

where $g_{tr}(r)$ is a trial multi-electron function with some free parameters. The trial functions may be chosen to correspond to a certain dissociation limit, and hence if two of these are decided upon (in the simplest case) then for another configuration of the nuclei the related electronic energies are independent of each other. In principle they could cross, i.e. become degenerate, for a particular configuration. More accurate trial function, however, is a combination of the Hartree-Fock ones, so called configuration interaction functions. In this case the minimization procedure of the kind (1.25) becomes the minimization of the eigenvalues of the matrix that is obtained from these configurations, say for two of these $g_{tr}^{(1)}(r)$ and $g_{tr}^{(2)}(r)$ it is given by

$$H = \begin{vmatrix} H_{1,1} & H_{1,2} \\ H_{2,1} & H_{2,2} \end{vmatrix}$$

¹⁰The Hartree-Fock method is far from being accurate for calculating energies of the electronic states, however, in here it is not used for this purpose but to demonstrate why these do not become degenerate. In short, to demonstrate the source of the avoided crossing of the electronic energies.

where

$$H_{i,j}(R) = \int d^{3N_{el}} r g_{tr}^{(i)}(r) [T_{el}(r) + V(r, R)] g_{tr}^{(j)}(r)$$

If the diagonal elements are degenerate at R_{deg} then in their vicinity one can write

$$H \approx \begin{vmatrix} H^{(0)} + (R - R_0) \cdot H_{1,1}^{(1)} & H_{1,2}^{(0)} \\ H_{2,1}^{(0)} & H^{(0)} + (R - R_0) \cdot H_{2,2}^{(1)} \end{vmatrix}$$

where

$$H_{i,j}^{(0)} = \int d^{3N_{el}} r g_{tr}^{(i)}(r) [T_{el}(r) + V(r, R_0)] g_{tr}^{(j)}(r),$$

$$(R - R_0) \cdot H_{1,1}^{(1)} = \sum_n^{3N_{nu}-3} (R_n - R_{n;0}) \int d^{3N_{el}} r g_{tr}^{(i)}(r) \nabla_{R_n} V(r, R_0) g_{tr}^{(j)}(r)$$

The eigenvalues are therefore

$$\lambda_{1,2} = \frac{1}{2} \left[2H^{(0)} + (R - R_0) \cdot (H_{1,1}^{(1)} + H_{2,2}^{(1)}) \right] \quad (1.26)$$

$$\pm \frac{1}{2} \sqrt{\left[(R - R_0) \cdot (H_{1,1}^{(1)} - H_{2,2}^{(1)}) \right]^2 + (\Delta H)^2}$$

where

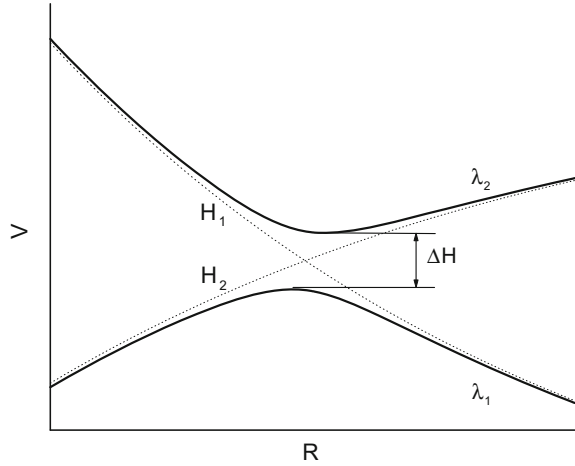
$$\Delta H = 2 \left| H_{1,2}^{(0)} \right|$$

and the electronic energies do not cross. The splitting is due to the “coupling” between the configuration interaction basis functions, and this effect on its own cannot be the sign of the breakdown of the adiabatic approximation. The breakdown is entirely due to the coupling that causes nuclei to change motion from one electronic energy state into another. Example of the avoided crossing of the electronic energies is shown in Fig. 1.3, where the diabatic electronic energies are indicated by H_1 and H_2 .

From the previous remarks one traces the cause of the breakdown of the adiabatic approximation to the matrix η because in the set of equations (1.24) it mixes the channels of different electronic states. This matrix, the coupling matrix among the electronic states, appears in the form of the first power and the second power. The latter could be neglected in the qualitative analysis, because η has only the off diagonal elements whilst η^2 has the diagonal ones as well, but especially in a two state problem when its off diagonal elements are zero. Therefore, the quadratic term does not contribute towards mixing of the electronic states, at least not in an essential way. This, however, is not always true as it will be shown later.

From the explicit expression (1.23) of the matrix elements of η mixing of the states starts when the eigenvalues $\lambda(R)$ are not well separated, i.e. when they are in the regime of the avoided crossing. The source of the avoided crossing was discussed, and as argued this happens in a relatively small interval around some isolated

Fig. 1.3 Electronic energies of two states in the regime of avoided crossing



configurations of the nuclei. Based on this finding it could be assumed that for the purpose of estimating the extent of mixing of the electronic states it is sufficient to analyze a two state problem. In this case the only non-zero elements of η are

$$\eta_{n;1,2}(R) = -\eta_{n;2,1}(R) = \frac{1}{\lambda_2(R) - \lambda_1(R)} \sum_{i,j=1}^2 U_{i,1} \langle i | V'_n(r, R) | j \rangle^{di} U_{j,2}$$

and in the vicinity of the avoided crossing the diabatic elements are (nearly) constant whilst the denominator has a functional dependence based on the estimate (1.26). The unitary matrix U parametrizes as

$$U = \begin{vmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{vmatrix}$$

in which case one derives

$$\eta_{n;1,2}(R) = \nabla_{R_n} \phi = \frac{1}{\lambda_2(R) - \lambda_1(R)} \left(\frac{V'_{n;1,1} - V'_{n;2,2}}{2} \sin 2\phi + V'_{n;1,2} \cos 2\phi \right)$$

where

$$V'_{n;i,j}(R) = \langle i | V'_n(r, R) | j \rangle^{di}$$

In the vicinity of crossing of the diabatic electronic states the matrix elements $V'_{n;i,j}(R)$ are nearly constant and could be fixed to have value the $V'_{n;i,j}(R_0)$. It follows from this, and the definition of the diabatic states, that $V'_{n;1,2} \approx 0$ and

$$V'_{n;1,1} - V'_{n;2,2} \approx H_{1,1}^{(1)} - H_{2,2}^{(1)}$$

hence the equation for the phase ϕ has a solution

$$\tan \phi = (R - R_0) \cdot Q + \sqrt{[(R - R_0) \cdot Q]^2 + 1}$$

where

$$Q_n = \frac{H_{n;1,1}^{(1)} - H_{n;2,2}^{(1)}}{\Delta H}$$

and the coupling matrix is

$$\eta_n = \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix} \nabla_{R_n} \phi = \frac{|Q_n|}{2} \frac{1}{[(R - R_0) \cdot Q]^2 + 1} \begin{vmatrix} 0 & 1 \\ -1 & 0 \end{vmatrix}$$

There are two limits to consider depending on the value of $|Q_n|$, the “coupling constants” among the electronic states, but in fact depending on ΔH . In one limit ΔH is very small in which case the coupling constants $|Q_n|$ are very large. The matrix η is in this case nearly a delta function and the set of equations (1.24), without the quadratic term in the same matrix, have a straightforward solution. The unitary matrix has a step-like property, on one side of the turning points R_0 it is, say, (nearly) a unit matrix and on the other side it is a matrix with the zero elements on the diagonal. This means, for example, that if on one side solution in a particular channel corresponds to the electron energy 1 on the other side it corresponds to the electron energy 2. This behavior is precisely that of a diabatic solution. However, obtaining this solution from the set (1.24) is not possible because the quadratic term in η is of the order of the square of a delta function, the singularity that is not integrable. In this case the adiabatic expansion fails, and hence the adiabatic approximation, the Born-Oppenheimer approximation, has no meaning. The way out is to transform the set (1.24) into the diabatic form when it could be solved by a perturbation method, say the distorted channel method. In this case one could define, by analogy, the diabatic approximation.

The other limit is when the coupling constants are small, i.e. when ΔH is large. In this case the matrix η is small and hence its quadratic form is smaller, and also $\nabla_{R_n} \eta_n(R)$ is negligible. The adiabatic approximation has meaning in this case and its corrections are calculated from the set (1.24) by a perturbation method.

In between these two extremes there is a transition region where one could say that the adiabatic approximation has meaning but it is not accurate. The details of how to analyze solution in this case is not elaborated here, this is a topic on its own.

1.3.2 Hydrogen Atom in Harmonic Oscillator

1.3.2.1 Classical Theory

Adiabatic approximation in a classical system is demonstrated on example of a proton being subject to a harmonic force and the electron is coupled to the proton by

Coulomb force. For simplicity the problem is treated in two dimensions. Equations to be solved are

$$\begin{aligned}\ddot{\vec{R}} &= -\omega^2 \vec{R} - \alpha \frac{m}{M} \frac{\vec{u}}{u^3} \\ \ddot{\vec{u}} &= -\alpha \left(1 + \frac{m}{M}\right) \frac{\vec{u}}{u^3} - \omega^2 \vec{R}\end{aligned}\quad (1.27)$$

where $\vec{R}$ is coordinate of the proton and $\vec{u}$ is connected with the coordinate of the electron $\vec{r}$ by $\vec{u} = \vec{R} - \vec{r}$. The coordinates and time are dimensionless, $\vec{R}$ and $\vec{u}$ stand for $\vec{R}\kappa$ and $\vec{u}\kappa$, respectively, whilst time t stands for $t\kappa$, where

$$\kappa = \frac{mc}{\hbar} = 2.58961 \times 10^{12} \text{ m}^{-1}$$

is Compton wave number for the electron. In the adiabatic approximation one neglects the terms of the order M^{-1} , which also includes ω^2 because it is of the same order of magnitude. The set of equations to solve is now

$$\begin{aligned}\ddot{\vec{R}}_{ad} &= -\omega^2 \vec{R}_{ad} \\ \ddot{\vec{u}}_{ad} &= -\alpha \frac{\vec{u}_{ad}(t)}{u_{ad}^3(t)} - \omega^2 \vec{R}_{ad}\end{aligned}$$

where α is the fine structure constant, which is defined as

$$\alpha = \frac{e^2}{4\pi\epsilon_0\hbar c} = \frac{1}{137.036}$$

Motion of proton is independent from that of the electron, whilst trajectory of the electron is parametrically dependent on the coordinates of the proton.

Solution for the adiabatic trajectory of the proton is

$$\vec{R}_{ad} = \vec{R}_0 \cos(\omega t + \delta) + \frac{1}{\omega} \vec{V}_0 \sin(\omega t + \delta)$$

and by assuming the simplest case, that the electron is in a circular orbit of the radius $1/\alpha$ (ground state Bohr orbit) around the proton, then its adiabatic trajectory is

$$\vec{u}_{ad}(t) = \vec{u}_0(t) - \frac{\omega^2}{\omega_{el}} \int_0^t d\tau \sin[\omega_{el}(t - \tau)] \vec{R}_{ad}(\tau) \quad (1.28)$$

where

$$\vec{u}_0(t) = \frac{1}{\alpha} [\hat{x} \cos(\omega_{el}t + \delta_{el}) + \hat{y} \sin(\omega_{el}t + \delta_{el})]$$

From the adiabatic solutions one calculates corrections, and of particular interest is correction to the trajectory of the proton. Solution for this trajectory is in direct relationship to what is the purpose of the Born-Oppenheimer approximation. Trajectory for the proton is solution of equation

$$\ddot{\vec{R}} = -\omega^2 \vec{R} - \alpha \frac{m}{M} \frac{\vec{u}_{ad}}{u_{ad}^3}$$

or in approximate form

$$\ddot{\vec{R}} \approx -\omega^2 \vec{R} - \alpha^4 \frac{m}{M} \vec{u}_{ad}(t)$$

where it is assumed that $u_{ad}^3 \approx u_0^3$. The equation has solution

$$\vec{R} = \vec{R}_{ad} - \frac{1}{\omega} \alpha^4 \frac{m}{M} \int_0^t d\tau \sin[\omega(t - \tau)] \vec{u}_{ad}(\tau)$$

and by replacing $\vec{u}_{ad}(t)$ with (1.28) one gets two integrals in the time variable. The integral that involves $\vec{u}_0(t)$ is straightforward to solve and solution is oscillatory, with the bounded amplitude. On the other hand the integral with the second term in (1.28) is

$$\vec{R} \approx \alpha^4 \frac{m\omega}{M\omega_{el}} \int_0^t d\tau \int_0^\tau ds \sin[\omega(t - \tau)] \sin[\omega_{el}(\tau - s)] \vec{R}_{ad}(s)$$

and its amplitude increases linearly in time. This result is of particular interest because it shows that expansion in the powers of $\frac{m}{M}$, at least in classical mechanics, may not be convergent.

1.3.2.2 Quantum Theory

Hydrogen atom that is subject to an external harmonic force is a good example where one could study interdependence of the electron and the proton motion. Classical study was done in Sect. 1.3.2 and here it will be shown how the problem is solved in quantum dynamics. Equation for this system, in the same scaling as in Sect. 1.3.2, is

$$\left(-\frac{q}{2} \Delta_R - \frac{1}{2} \Delta_r + \frac{1}{2q} w^2 R^2 - \frac{\alpha}{|\vec{r} - \vec{R}|} \right) f(\vec{R}, \vec{r}) = E f(\vec{R}, \vec{r}) \quad (1.29)$$

which is solved by writing solution as expansion

$$f(\vec{R}, \vec{r}) = \sum_n g_n(\vec{R}) h_n(\vec{r} - \vec{R})$$

where $h_n(\vec{r})$ is solution of equation

$$\left(-\frac{1}{2} \Delta_r - \frac{\alpha}{|\vec{r} - \vec{R}|} \right) h_n(\vec{r} - \vec{R}) = e_n h_n(\vec{r} - \vec{R}) \quad (1.30)$$

As before one chooses the parameter $q = m/M$ as the measures of quality for adiabatic expansion. When the expansion is replaced in (1.29) one obtains a set of equations for the functions $g_n(\vec{R})$, which is in a matrix form given by

$$\begin{aligned} -\frac{q}{2} (\nabla_R - \langle h | \nabla h \rangle)^2 g + \frac{1}{2q} w^2 R^2 g + \frac{q}{2} (\langle h | \nabla h \rangle^2 - \langle h | \Delta | h \rangle) g \\ = (E - e) g \end{aligned} \quad (1.31)$$

where in derivation equation (1.30) was used. The matrix elements are defined as

$$[\langle h | \nabla h \rangle]_{i,j} = \int d^3r h_i(\vec{r}) \nabla h_j(\vec{r})$$

and e is diagonal matrix.

Ratio of the two masses q appears in the part of the set (1.31) that refers to the motion of the centre of mass of Hydrogen (proton) and also in the term that couples it to the motion of the electron (the last term on the left). It would appear that by neglecting this ratio the two motions would be decoupled, which would indeed be the case if it is not that the coupling also appears in the kinetic energy of the Hydrogen. Therefore, in addition to neglecting the ratio of the two masses it should be assumed that momentum of the heavier mass, the average of ∇_R , is much larger than the average of momentum of the lighter one $\langle h | \nabla h \rangle$. This approximation, however, may not be the sole criterion, if the energy difference in e is very large then by replacing g with

$$g = e^{\vec{R} \cdot \langle h | \nabla h \rangle} f$$

then (1.31) is approximately

$$-\frac{q}{2} \nabla_R^2 f + \frac{1}{2q} w^2 R^2 f = (E - e) f$$

The equation describes entirely de-coupled motion of the atom from that of the electron.

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