

Appendix 2.D

The van der Waals interaction

materiale data

studenti
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①

Historically one can distinguish two contributions to the van der Waals interaction:^{1*)}

1) dispersive (retarded) contribution^{2**)}, emerging from the dynamical dipole-dipole, as well as from higher multipolarities, interaction associated with the quantum mechanical zero point fluctuations (ZPF) of the ground state of the two interacting atoms or molecules associated with the dipole excitations of the systems^{3***)}

2) inductive implying the polarization of one molecule in the permanent dipole or quadrupole field of the other molecule^{4**)} (see P. Debye, Phys. Z. 21 (1920) 178; 22 (1921) 302)

It is only the first one which is a bona fide van der Waals interaction. In fact with the advent of quantum mechanics it was very early recognized^{5*)} (London, F. (1930))

Z. f. Physik 63, 245) that for most molecules interactions of type 2) are small compared with interactions of type 1), that is the interaction corresponding to the mutual polarization of one molecule in the rapidly changing field (due to the instantaneous configuration of electrons and nuclei) of the other molecule^{6*)} (cf. also L. Pauling and E.B. Wilson Jr. Quantum Mechanics, Dover, New York (1963) p. 383)

1*) Let us mainly think of non polar (NP) molecules

2**) dispersion: variation of a quantity, e.g., spatial separation of white light (rainbow), as a function of frequency (cf. e.g. J.N. Israelachvili, Intermolecular and Surface forces, Academic press, New York (1985) p. 65)

3*** These forces - like the gravitational force - act between all atoms and molecules, even non-polar, totally neutral ones as hydrogen or helium (noble gas).

4*) ✓

5*) ↑

6*) ←

Within the framework of the theories of systems with many degrees of freedom (i.e. fields- and (many-body) - systems) developed in particular by Anderson, Nambu and Goldstone, it has been recognized that that the phenomenon of spontaneous symmetry breaking is at the basis of physical emergent properties (see App)

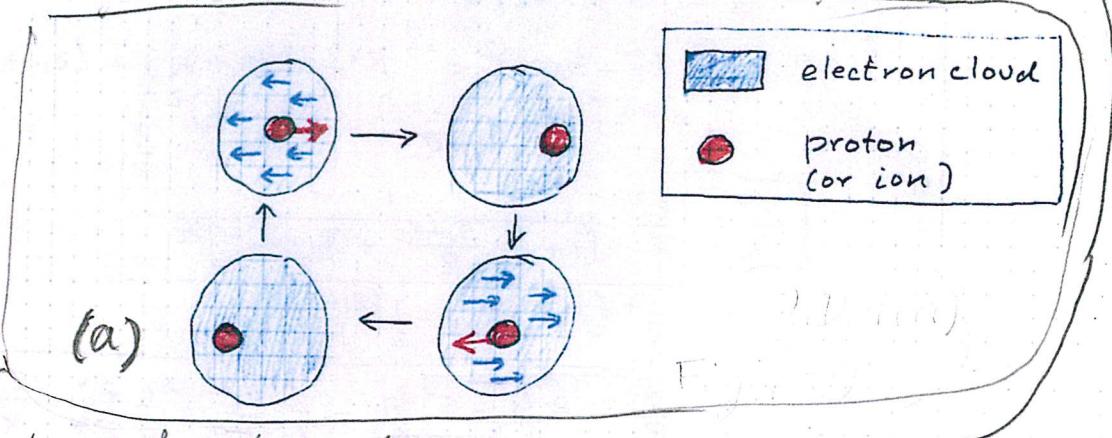
Within the present context, an atom (i.e. a E) relates translational invariance as its center of mass (CM) occupies a definite position in space defining a privileged origin for a reference frame. Setting both ions and electrons in uniform motion, through a Galilean transformation, restores symmetry, the inertia being the total mass. Thus the system moves as a rigid body (generalized rigidity, no need of propagation of information through it).

Such a motion (isoscalar in the case of the atomic nuclei, where N and Z move in phase, equivalent to electrons and ions doing so in the case of condensed or soft matter) display zero restoring force. Thus, the associated ZPF diverge requiring, quantum mechanically, a state orthogonal to it in which the two types of constituents particles (electrons and ions, and neutrons and protons), move out of phase. Such a state is, in the nuclear case^{7*)} the GDR and corresponds to a mode in which protons and neutrons slosh back and forth out of phase (isovector mode), a situation which is similar to that of atomic clusters (Mie resonance, see Figs. 1(a) and 1(b) pp. (3) and (4)). In the atomic or molecular case these states (dipole vibration of electrons against the

^{7*)} Note however the newly discovered pigmy halo resonance (soft E1-mode in neutron halo nuclei like ^{11}Li , which essentially forces a permanent dipole in the $|^{11}\text{Li}(\text{gs})\rangle$), which can thus be viewed as a rotation of the dipole moment, like e.g. in water molecules, although it is a large amplitude, plastic dipole vibration.

(3)

positive ions) are rather directly related to the single-electron atomic shell physics ($1s \rightarrow 2p$ transition in the case of H atom). The associated ZPF being displayed in Fig. 2.D.1(a).



in terms of a cartoon

Two atoms displaying the above ZPF will interact through & Van der Waals (dispersive, retarded) interaction (Fig. 2.D.1(b)).

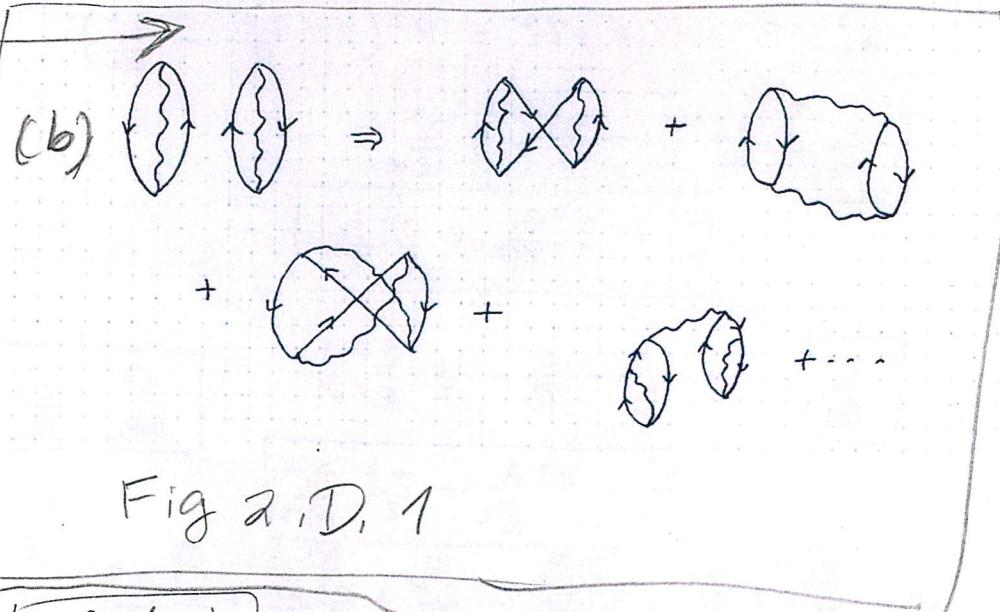


Fig 2.D.1

That is,

positive ions)
The associated ZPF - - -

in term of a cartoon: Two atoms ...
retarded) interaction (Fig. 2.D.1(b))

gregory

asi se tiene
que ver
esta pagina

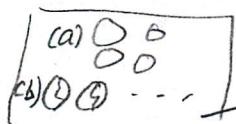
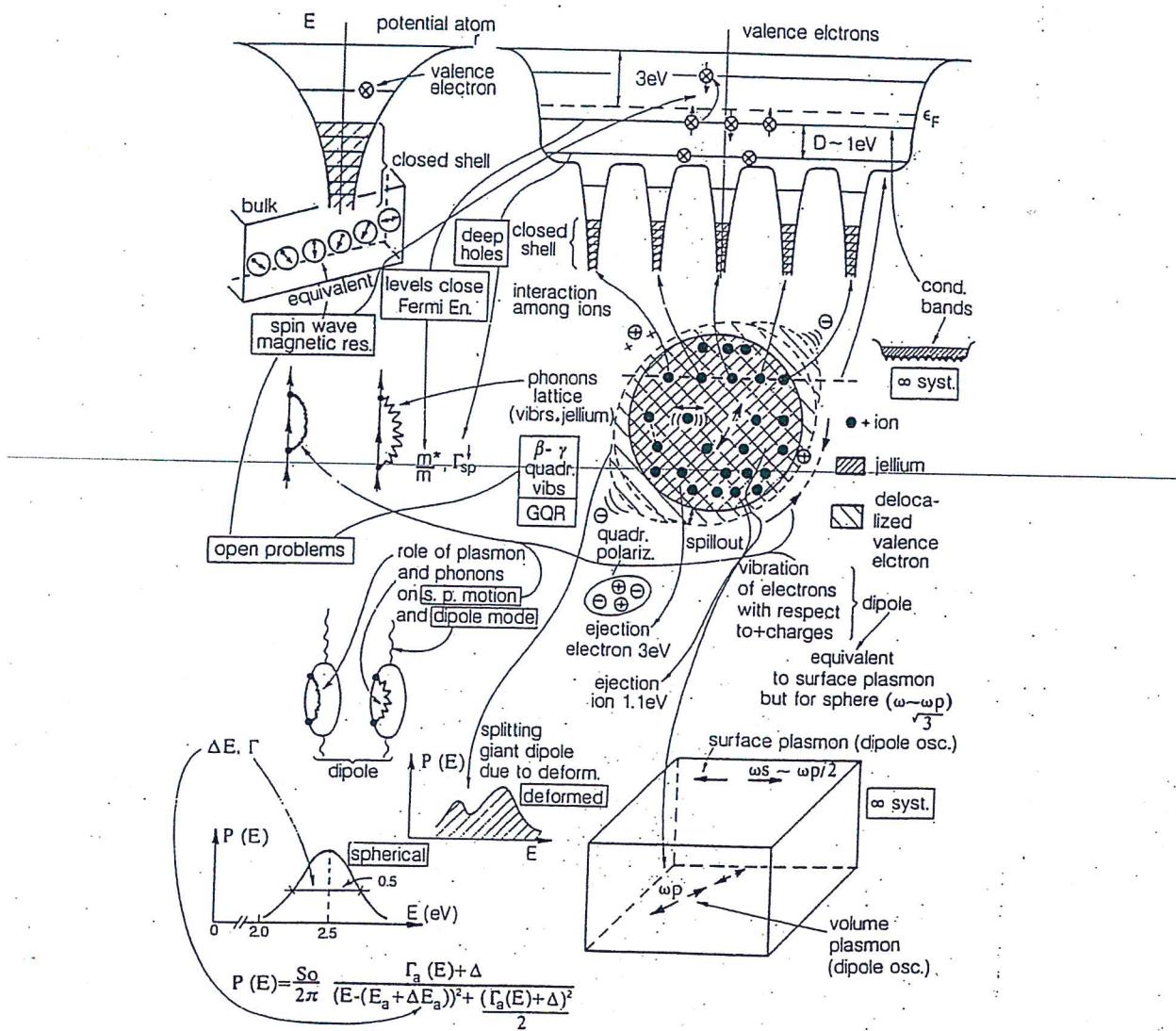


Fig. 2.D.1. (a) Dipole ZPF associated with an atom. (b) van der Waal interaction (dispersive contribution).



2.D.2

Fig. 101 Schematic representation concerning the response to photons of both nuclei and metal clusters after Broglia et al Prog. Part. Nucl. Phys. 28 (1992) pp 517-527.

2.D.1

van der Waals interaction between two hydrogen atoms (Pauling and Wilson (1963) p. 383)

For large values of the internuclear distance $r_{AB} = R$, the exchange phenomenon is unimportant (Pauli principle) and one can take as the unperturbed wavefunction for a system of two hydrogen atoms ^(Fig. 2.D.3) the simple product of two hydrogenlike wavefunctions,

$$\Psi^0 = u_{1sA}(1) u_{1sB}(2) \quad (1) \quad (2.D.1)$$

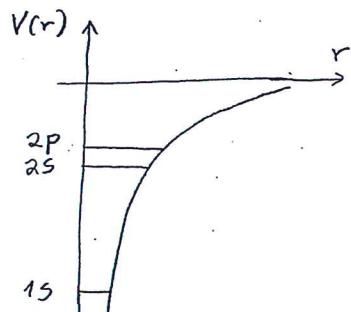


Fig. 2

Fig. 2.D.3

The perturbation for this wavefunction arises from the potential energy terms

$$H' = \frac{e^2}{r_{12}} + \frac{e^2}{r_{AB}} - \frac{e^2}{r_{A2}} - \frac{e^2}{r_{B1}}, \quad (2.D.2)$$

corresponding to the Coulomb interaction between the atoms. Let us assume for

simplicity that we are dealing with a one-dimensional problem, in which case one can write (Fig. 2.D.4)

$$\vec{r}_{12} = (R + z_1 + z_2) \hat{z},$$

$$\vec{r}_{AB} = R \hat{z},$$

$$\vec{r}_{A2} = (R + z_2) \hat{z},$$

$$\vec{r}_{B1} = (R + z_1) \hat{z}.$$

Because all these distances are much larger than the radius of the atom ($a_0 \approx 0.529 \text{ \AA}$, Bohr radius) the expression (2) can be calculated

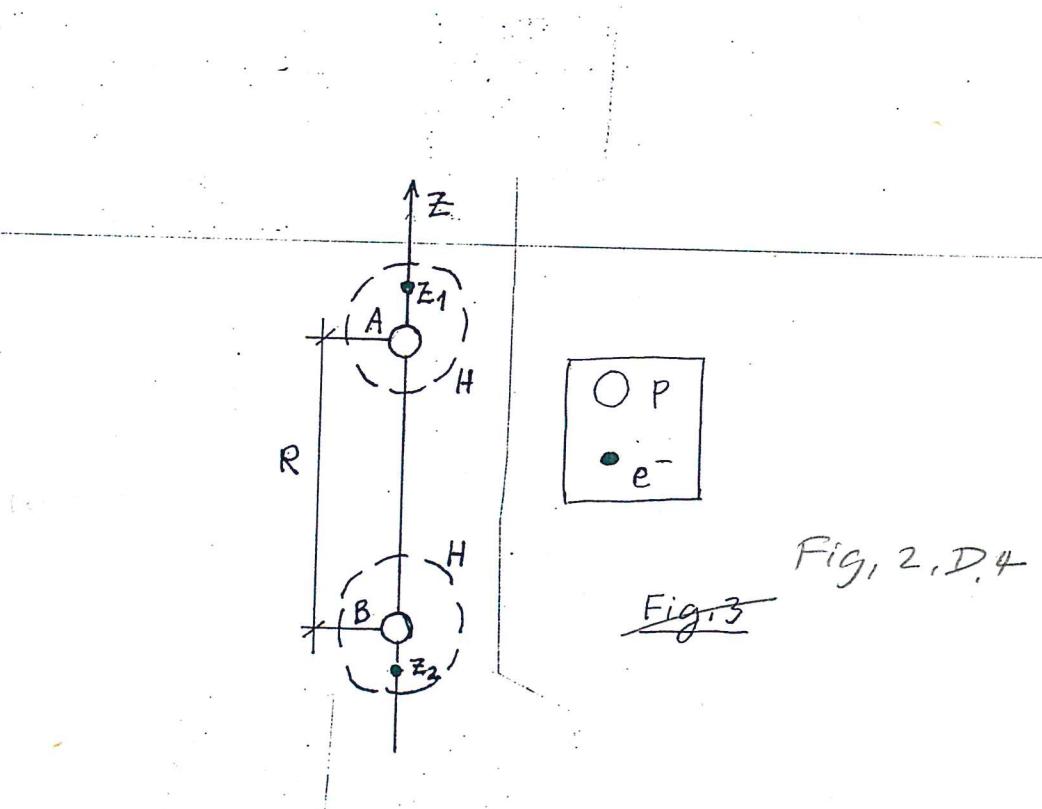


Fig. 2.D.4

Fig. 3

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(7)

making use of a Taylor expansion,
and diagonalize it with the help of
perturbation theory.

One obtains

$$r_{12}^2 = (R + z_1 + z_2)^2 = R^2 \left[1 + 2 \frac{(z_1 + z_2)}{R} + \frac{(z_1 + z_2)^2}{R^2} \right]$$

which leads to

$$\begin{aligned} \frac{e^2}{r_{12}} &= \frac{e^2}{R \left[1 + 2 \frac{(z_1 + z_2)}{R} + \frac{(z_1 + z_2)^2}{R^2} \right]^{1/2}} \\ &\approx \frac{e^2}{R} \left[1 - \frac{(z_1 + z_2)}{R} - \frac{(z_1 + z_2)^2}{2R^2} \right], \quad (2.D.2) \end{aligned}$$

Similarly

$$r_{A2}^2 = (R^2 + 2Rz_2 + z_2^2) = R^2 \left(1 + 2 \frac{z_2}{R} + \frac{z_2^2}{R^2} \right),$$

and

$$r_{B1}^2 = R^2 \left(1 + 2 \frac{z_1}{R} + \frac{z_1^2}{R^2} \right),$$

leading to

$$-\frac{e^2}{r_{A2}} = -\frac{e^2}{R} \left(1 - \frac{z_2}{R} - \frac{1}{2} \frac{z_2^2}{R^2} \right), \quad (2.D.3)$$

and

$$-\frac{e^2}{r_{B1}} = -\frac{e^2}{R} \left(1 - \frac{z_1}{R} - \frac{1}{2} \frac{z_1^2}{R^2} \right). \quad (2.D.4)$$

Finally

$$\frac{e^2}{r_{AB}} = \frac{e^2}{R}. \quad (2.D.5)$$

With the exception of the cross term of (2), there is complete cancellation between the different contributions to (2)-(5). Thus

$$H' = - \frac{\vec{D}_1 \cdot \vec{D}_2}{R^3}, \quad (6) \quad (2,D,6)$$

where

$$\vec{D}_i = e z_i \hat{z} \quad (7) \quad (2,D,7)$$

is the dipole moment operator associated with electron i . Because $R \gg z_i$, one can diagonalize the interaction Hamiltonian (6) perturbatively. Because a single-particle quantum state displaying a given parity (and in the present case angular momentum $(-1)^l = \pi$) cannot sustain a permanent dipole moment, in particular

$$\int d\sigma u_{1s}(z) \pm u_{1s}(z) = \int d\sigma (u_{1s}(z))^2 z = \int d\sigma p(z) z = 0, \quad (2,D,8)$$

the lowest perturbative correction to (4) is of second order. This is in keeping with the fact that we are dealing with interaction through virtual processes. The associated energy correction is given by the relation,

$$\Delta E_z^{(2)} = - \sum_{\text{int}} \frac{\langle 0 | H' | \text{int} \rangle \langle \text{int} | H' | 0 \rangle}{E_{\text{int}} - E_0}. \quad (9) \quad (2,D,9)$$

Because the $1s \rightarrow 2p$ transition (Fig. 2,D,5), we are concerned with

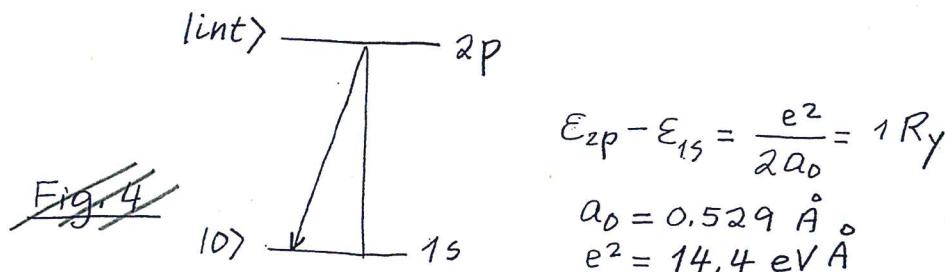
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(9)

$$\psi^{int} = u_{2pA}(1) u_{2pB}(2), \quad (10) \quad (z, D, 10)$$

and thus

$$Den = E_{int} - E_0 = \frac{e^2}{2a_0} = 1 Ry = 13.606 \text{ eV} \quad (11)$$



$$E_{2p} - E_{1s} = \frac{e^2}{2a_0} = 1 Ry$$

$$a_0 = 0.529 \text{ \AA}$$

$$e^2 = 14.4 \text{ eV \AA}$$

Fig. 2,D,5

One can then write

$$\begin{aligned} \Delta E_z^{(2)} &= -\frac{|\langle 0|H'|10\rangle|^2}{Den} = -\frac{e^4}{R^6} \frac{\langle 0|z_1^2 z_2^2|10\rangle}{Den} \quad (12) \\ &= -\frac{e^4}{R^6} \frac{\int d\sigma_1 d\sigma_2 u_{1s}^2(1) u_{1s}^2(2) z_1^2 z_2^2}{Den} \\ &= -\frac{e^4}{R^6} \frac{\int d\sigma_1 P(z_1) z_1^2 \int d\sigma_2 P(z_2) z_2^2}{Den} \quad (12) \\ &= -\frac{e^4}{R^6} \frac{\bar{z}_1^2 \bar{z}_2^2}{Den} = -\frac{e^4}{R^6} \frac{a_0^2 a_0^2}{\frac{e^2}{2a_0}} = -\frac{2e^2 a_0^5}{R^6} \quad (2, D, 12) \end{aligned}$$

This result corresponds to the z -degree of freedom of the system (two H atoms)

atoms at a distance $R \gg a_0$), one has thus to multiply the above result by 3 to take into account the x and y degrees of freedom. Thus

$$\Delta E^{(2)} = -\frac{6e^2 a_0^5}{R^6} . \quad (13) \quad (2.D.13)$$

Let us ^{now} calculate the van der Waals interaction between two H-atoms at a distance of the order of ten times the summed radii of the two atoms ($\approx 2a_0 \approx 1\text{\AA}$), that is for $R = 10\text{\AA}$,

$$\begin{aligned} \Delta E_{H-H}^{(2)}(10\text{\AA}) &\approx -\frac{6 \times 14.4 \text{ eV\AA} (0.529\text{\AA})^5}{(10\text{\AA})^6} \\ &\approx -3.6 \times 10^{-6} \text{ eV} = -3.6 \mu\text{eV} \end{aligned}$$

Making use of the relation (14) (2.D.14)

$$1\text{eV} = 2.42 \times 10^{14} \text{ Hz} , \quad (1\text{Hz} = \text{s}^{-1})$$

One obtains

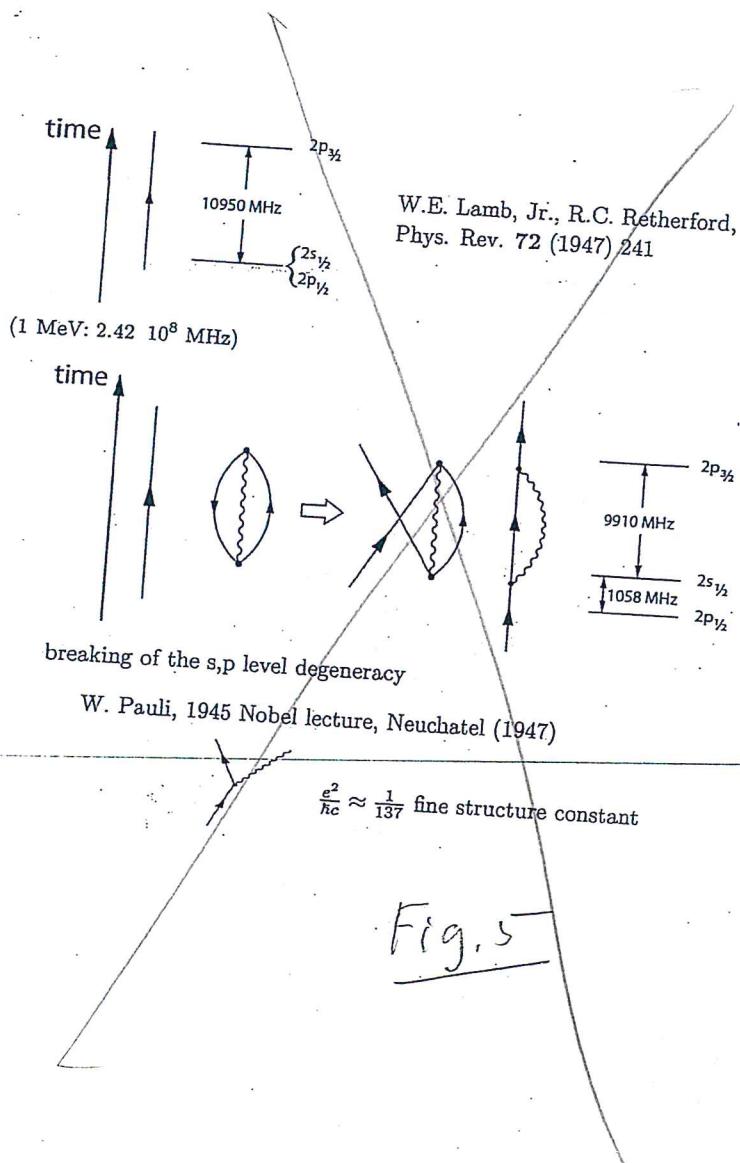
$$\begin{aligned} |\Delta E_{H-H}^{(2)}(10\text{\AA})| &\approx 3.6 \times 10^{-6} \times 2.42 \times 10^{14} \text{ Hz} \quad (2.D.15) \\ &\approx 9 \times 10^8 \text{ Hz} \approx 10^3 \text{ MHz}, \end{aligned}$$
Appendix 4.D; see also Fig. 6.2.1)

a quantity which can be compared with the Lamb shift (see Fig. 5, see also Fig. 1). Notice that $|\Delta E_{H-H}^{(2)}(2.5\text{\AA})| \approx 15 \text{ meV/part} \approx 0.35 \text{ kcal/mol}$, ($1 \text{ meV/part} \approx 0.02306 \text{ kcal/mol}$), a value of about $1/2 kT$.

It is of

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(11)



2D.2 Critical dimension for van der Waals H-H interaction (protein folding domain)

Let us calculate the frequency associated with the $1s \rightarrow 2p$ transition ($= 1 Ry = 13.6 \text{ eV}$),

$$\hbar\omega_e = 13.6 \text{ eV.} \quad (16) \quad (2.D.16)$$

Making use of

$$\hbar c = 2000 \text{ eV}\text{\AA}, \quad (17) \quad (2.D.17)$$

one can write

$$\omega_e = \frac{13.6 \text{ eV}}{\hbar c} c \approx 10^{-2} \text{\AA}^{-1} \text{ e.} \quad (18) \quad (2.D.18)$$

Now, the exchange of "information" between the ZPF of the two H-atoms must be faster than the electronic revolution period, namely

(2.D.19)

$$\frac{2R}{c} \ll \frac{1}{\omega_e} \quad (19)$$

In other words,

Fig 2.D.6



leading to

$$R \leq 50 \text{ fm.}$$

Otherwise the frequencies of the two periodic motions (ZPF based dipole-dipole interaction and orbiting of electron around proton) would be similar and a strong coupling between the two periodic motions would take place. In other words, there would be a strong damping of the retarded, dispersive contribution to the van der Waals interaction.

If this is so, and in keeping with the fact that the dimensions of an amino acid are, in average, 0.36 nm , the typical distance between two residues in a protein in its native state thus being $\approx 10\text{ \AA}$, one would expect the maximum number of amino acids of globular protein or of a folding domain, to be of the order of $(50\text{ \AA}/10\text{ \AA})^3 \approx 125$, as empirically observed.

2,D,3 van der Waals between two amino acids

All of the commonly occurring amino acids in proteins have a central carbon atom (C_α) to which are attached a hydrogen atom, an amino group (NH_2), and a carboxy ($COOH$). What distinguishes one amino acid from another is the side chain attached to the C_α through its fourth valency. There are 20 different side chains specified by the genetic code (Fig. 8). 2,D,7

Amino acids are joined end to end during protein synthesis by the formation of peptide bonds. The carboxyl group of the first amino acid condenses with the amino group of the next to eliminate water, thus the name residue, and yield a peptide bond.

The van der Waals interaction between two amino acids is,

$$\Delta E^{(2)} = -\frac{6Z^2e^2(a_0)^5}{R^6} \quad (2D)$$

where Z is the number of protons of the molecule.

3.D.4 Average interaction between two side chains

Typical dimension of an amino acid is $0.36 \text{ nm} (= 3.6 \text{ \AA})$. Let us then estimate the average van der Waals interaction of two residues at $R = 8 \text{ \AA}$. For this purpose use is made of $30 \leq Z \leq 35$ (Fig. 2.17). Thus one can then write,

$$\Delta E_{\text{aa}}^{(2)} = - \frac{6 \times Z^2 \times 14.4 \text{ eV \AA} (0.529 \text{ \AA})^5}{(8 \text{ \AA})^6}$$

$$= \begin{cases} -12.3 \frac{\text{meV}}{\text{part}} = -0.28 \frac{\text{kcal}}{M}, \\ -16.7 \frac{\text{meV}}{\text{part}} = -0.38 \frac{\text{kcal}}{M}, \end{cases} \quad (21)$$

Thus

(2.1.22)

$$\overline{\Delta E}_{\text{aa}}^{(2)}(8 \text{ \AA}) \approx -0.33 \frac{\text{kcal}}{M}, \quad (22)$$

a quantity to be compared to

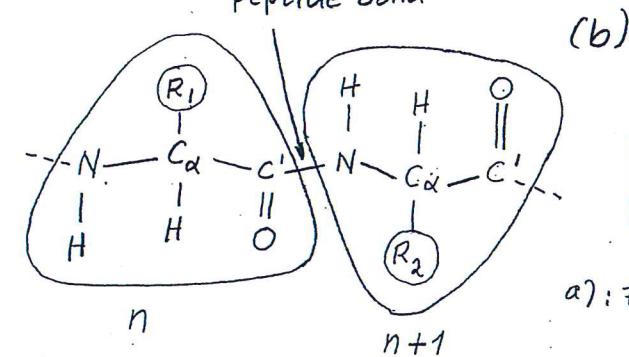
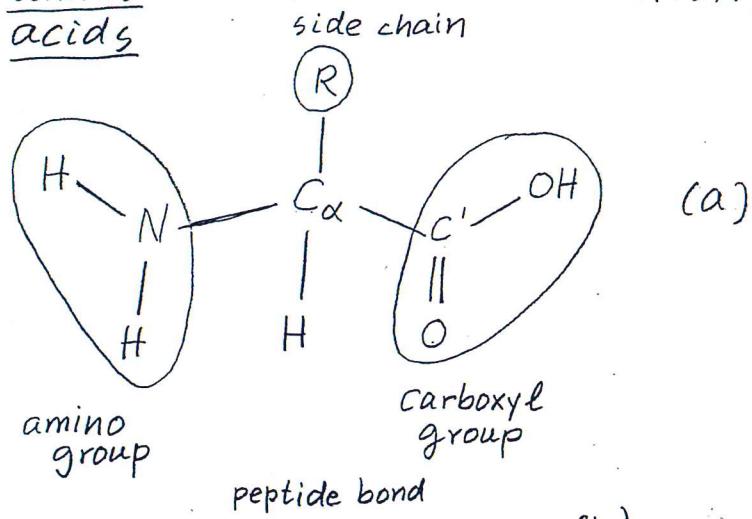
$$kT = 0.6 \text{ kcal/M}$$

Summing up, the van der Waals interaction between amino acids is weak, of the order of $kT/2 (\approx 0.3 \text{ kcal/M})$, with a range $\lesssim 0.5 \text{ nm}$, and non-directional.

amino acids

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(16)



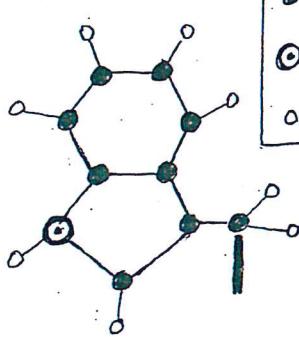
<u>backbone</u>	
# atoms	heavy atoms
6	4
29 ^{a)}	27 ^{a)}

a): # of protons

side chains

examples

	# atoms	heavy atoms
Glycine, Gly, G	prots. 1	0



Tryptophan, Trp, W (d)

	# atoms	heavy atoms
	18 protons 69	10 61

protons gross average $\frac{69+1}{2} = 35$; $\frac{61+0}{2} = 30$

2, D, 7

Fig 7

detailed calculation
total average
protons 36

(e)

Hindsight

The van der Waals interaction is closely related to the restoration of spontaneous symmetry breaking of translational invariance (center of mass of finite systems like atoms and molecules define privileged points in the otherwise homogeneous and isotropic vacuum), through ZPF of iscalar and isovector character, some of which diverge although retaining a finite inertia (mass of the system and associated emergent property, namely rigidity, pushing model; sloshing back and forth of opposite charges with very different spatial distributions (protons and electrons) thus essentially leading to a ground state displaying a permanent dipole^{moment}). Of notice that a similar phenomenon is found in atomic nuclei, in the case of light exotic halo neutron dripline systems like e.g. $^{11}\text{Li}_{\infty}$ (App. 2.B).