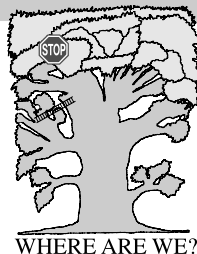


Chapter 12

THE MOLECULE IN AN ELECTRIC OR MAGNETIC FIELD



Where are we?

We are already in the crown of the TREE (left-hand side)

An example

How does a molecule react to an applied electric field? How do you calculate the changes it undergoes? In some materials there is a strange phenomenon: a monochromatic *red* laser light beam enters a transparent substance, and leaves the specimen as a *blue* beam. Why?

Another example, this time with a magnetic field. We apply a long wavelength electromagnetic radiation to a specimen. We do not see any absorption whatsoever. However, if, in addition, we apply a static magnetic field gradually increasing in intensity, at some intensities we observe absorption. If we analyze the magnetic field values corresponding to the absorption then they cluster into mysterious groups that depend on the chemical composition of the specimen. Why?

What is it all about

The properties of a substance with and without an external electric field *differ*. The problem is how to compute the molecular properties in the electric field from the properties of the isolated molecule and the characteristics of the applied field. Molecules react also upon application of a magnetic field, which changes the internal electric currents and modifies the local magnetic field. A nucleus may be treated as a small magnet, which reacts to the local magnetic field it encounters. This local field depends not only on the external magnetic field, but also on those from other nuclei, and on the electronic structure in the vicinity. This produces some energy levels in the spin system, with transitions leading to the nuclear magnetic resonance (NMR) phenomenon which has wide applications in chemistry, physics and medicine.

The following topics will be described in the present chapter.

Helmann–Feynman theorem

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ELECTRIC PHENOMENA

p. 620

The molecule immobilized in an electric field (♦§)

p. 620

- The electric field as a perturbation
- The homogeneous electric field
- The inhomogeneous field: multipole polarizabilities and hyperpolarizabilities

How to calculate the dipole moment? (♦§)

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• Hartree–Fock approximation	
• Atomic and bond dipoles	
• Within the ZDO approximation	
How to calculate the dipole polarizability? (◆Ⓢ)	p. 635
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MAGNETIC PHENOMENA	p. 647
Magnetic dipole moments of elementary particles (◆Ⓢ)	p. 648
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The Ramsey theory of the NMR chemical shift (◆Ⓢ)	p. 666
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• Coupling constants	
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Why is this important?

There is no such a thing as an isolated molecule, since any molecule interacts with its neighbourhood. In most cases this is the electric field of another molecule or an external electric field and represents the only information about the external world the molecule has. The source of the electric field (another molecule or a technical equipment) is of no importance. *Any molecule will respond to the electric field, but some will respond dramatically, while others may respond quite weakly.* This is of importance in designing new materials.

The molecular electronic structure does not respond to a change in orientation of the nuclear magnetic moments, because the corresponding perturbation is too small. On the other hand, the molecular electronic structure influences the subtle energetics of interaction of the nuclear spin magnetic moments and these effects may be recorded in the NMR spectrum. This is of great practical importance, because it means *we have in the molecule un-*

der study a system of sounds (nuclear spins) which characterize the electronic structure almost without perturbing it.

What is needed?

- Perturbation theory (Chapter 5, necessary).
- Variational method (Chapter 5, advised).
- Harmonic oscillator and rigid rotator (Chapter 4, advised).
- Breit Hamiltonian (Chapter 3, advised).
- Appendix S, p. 1015 (advised).
- Appendix G, p. 962 (necessary for magnetic properties).
- Appendix M, p. 986 (advised).
- Appendix W, p. 1032 (advised).

Classical works

Peter Debye, as early as 1921, predicted in “*Molekularkräfte und ihre Elektrische Deutung*”, *Physikalische Zeitschrift*, 22 (1921) 302 that a non-polar gas or liquid of molecules with a non-zero quadrupole moment, when subject to an inhomogeneous electric field, will exhibit the birefringence phenomenon due to the orientation of the quadrupoles in the electric field gradient. ★ The book by John Hasbrouck Van Vleck “*Electric and Magnetic Susceptibilities*”, Oxford University Press, 1932 represented enormous progress. ★ The theorem that forces acting on nuclei result from classical interactions with electron density (computed by a quantum mechanical method) was first proved by Hans Gustav Adolf Hellmann in the world’s first textbook of quantum chemistry “*Einführung in die Quantenchemie*”, Deuticke, Leipzig und Wien,¹ (1937), p. 285, and then, independently, by Richard Philips Feynman in “*Forces in Molecules*” published in *Physical Review*, 56 (1939) 340. ★ The first idea of nuclear magnetic resonance (NMR) came from a Dutch scholar, Cornelis Jacobus Gorter, in “*Negative Result in an Attempt to Detect Nuclear Spins*” in *Physica*, 3 (1936) 995. ★ The first *electron* paramagnetic resonance (EPR) measurement was carried out by Evgenii Zavoiski from Kazan University (USSR) and reported in “*Spin-Magnetic Resonance in Paramagnetics*” published in *Journal of Physics (USSR)*, 9 (1945) 245, 447. ★ The first NMR absorption experiment was performed by Edward M. Purcell, Henry C. Torrey and Robert V. Pound and published in “*Resonance Absorption by Nuclear Magnetic Moments in a Solid*”, which appeared in *Physical Review*, 69 (1946) 37, while the first correct explanation of nuclear spin–spin coupling (through the chemical bond) was given by Norman F. Ramsey and Edward M. Purcell in “*Interactions between Nuclear Spins in Molecules*” published in *Physical Review*, 85 (1952) 143. ★ The first successful experiment in non-linear optics with frequency doubling was reported by Peter A. Franken, Alan E. Hill, Wilbur C. Peters and Gabriel Weinreich in “*Generation of Optical Harmonics*” published in *Physical Review Letters*, 7 (1961) 118. ★ Hendrik F. Hameka’s book “*Advanced Quantum Chemistry. Theory of Interactions between Molecules and Electromagnetic Fields*” (1965) is also considered a classic work. ★ Although virtually unknown outside Poland, the book “*Mole-*

John Hasbrouck Van Vleck (1899–1980), American physicist, professor at the University of Minnesota, received the Nobel Prize in 1977 for “*fundamental theoretical investigations of the electronic structure of magnetic and disordered systems*”.



¹A Russian edition had appeared a few months earlier, but it does not contain the theorem.

cular Non-Linear Optics”, Warsaw–Poznań, PWN (1977) (in Polish) by Stanisław Kielich, deserves to be included in the list of classic works.

12.1 HELLMANN–FEYNMAN THEOREM

Let us assume that a system with Hamiltonian \hat{H} is in a *stationary state* described by the (normalized) function ψ . Now let us begin to do a little “tinkering” with the Hamiltonian by introducing a parameter P . So we have $\hat{H}(P)$, and assume we may change the parameter smoothly. For example, as the parameter P we may take the electric field intensity, or, if we assume the Born–Oppenheimer approximation, then as P we may take a nuclear coordinate.² If we change P in the Hamiltonian $\hat{H}(P)$, then we have a response in the eigenvalue $E(P)$. The eigenfunctions and eigenvalues of \hat{H} become functions of P .

Hans Gustav Adolf Hellmann (1903–1938), German physicist, one of the pioneers of quantum chemistry. He contributed to the theory of dielectric susceptibility, theory of spin, chemical bond theory (semiempirical calculations, also virial theorem and the role of kinetic energy), intermolecular interactions theory, electronic affinity, etc. Hellmann wrote the world's first textbook of quantum chemistry “*Vvedeniye v kvantovuyu khimiyu*”, a few months later edited in Leipzig as “*Einführung in die Quantenchemie*”. In 1933 Hellmann presented his habilitation thesis at the Veterinary College of Hannover. As part of the paper work he filled out a form, in which according to the recent Nazi requirement he wrote that his wife was of Jewish origin. The Nazi ministry rejected the habilitation. The situation grew more and more dangerous (many students of the School were active Nazis) and the Hellmanns decided to emigrate. Since his wife originated from the Ukraine they chose the Eastern route. Hellmann obtained a position at the Karpov Institute of Physical Chemistry in Moscow as a theoretical group leader. A leader of another group, the Communist Party First Secretary of the Institute (Hellmann's colleague and a co-author of one of his papers) A.A. Zukhovitsky as well as the former First Secretary, leader of the Heterogenic Catalysis Group Mikhail Tiomkin, denounced Hellmann to the institution later called the KGB, which soon arrested



him. Years later an investigation protocol was found in the KGB archives, with a text about Hellmann's spying written by somebody else but with Hellmann's signature. This was a common result of such “investigations”. On May 16, 1938 Albert Einstein, and on May 18 three other Nobel prize recipients: Irene Joliot-Curie, Frederick Joliot-Curie and Jean-Baptiste Perrin, asked Stalin for mercy for Hellmann. Stalin ignored the eminent scholars' supplication, and on May 29, 1938 Hans Hellmann faced the firing squad and was executed.

After W.H.E. Schwarz et al., *Bunsen-Magazin* (1999) 10, 60. Portrait reproduced from a painting by Tatiana Livschitz, courtesy of Professor Eugen Schwarz.

²Recall please that in the adiabatic approximation, the electronic Hamiltonian depends parametrically on the nuclear coordinates (Chapter 6). Then $E(P)$ corresponds to $E_k^0(R)$ from eq. (6.8).

Richard Philips Feynman (1919–1988), American physicist, for many years professor at the California Institute of Technology. His father was his first informal teacher of physics, who taught him the extremely important skill of independent thinking. Feynman studied at Massachusetts Institute of Technology, then in Princeton University, where he defended his Ph.D. thesis under the supervision of John Archibald Wheeler.



From John Slater's autobiography "*Solid State and Molecular Theory*", London, Wiley (1975):

"... The theorem known as the Hellmann–Feynman theorem, stating that the force on a nucleus can be rigorously calculated by electrostatics (...), remained, as far as I was concerned, only a surmise for several years. Somehow, I missed the fact that Hellmann, in Germany, proved it rigorously in 1936, and when a very bright undergraduate turned up in 1938–1939 wanting a topic for a bachelor's thesis, I suggested to him that he see if it could be proved. He come back very promptly with a proof. Since he was Richard Feynman (...), it is not surprising that he produced his proof without trouble."

In 1945–1950 Feynman served as a professor at Cornell University. A paper plate thrown in the air by a student in the Cornell cafe was the first impulse for Feynman to think about creating a new version of quantum electrodynamics. For this achievement Feynman received the Nobel prize in 1965, cf. p. 14.

Feynman was a genius, who contributed to several branches of physics (superfluidity, weak interactions, quantum computers, nanotechnology). His textbook "*The Feynman Lectures on Physics*" is considered an unchallenged achievement in academic literature. Several of his books became best-sellers. Feynman was famous for his unconventional, straightforward and crystal-clear thinking, as well as for his courage and humour. Curiosity and courage made possible his investigations of the ancient Maya calendar, ant habits, as well as his activity in painting and music.

The Hellmann–Feynman theorem pertains to the rate of the change³ of $E(P)$:

HELLMANN-FEYNMAN THEOREM:

$$\frac{\partial E}{\partial P} = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial P} \right| \psi \right\rangle. \quad (12.1)$$

The proof is simple. The differentiation with respect to P of the integrand in $E = \langle \psi | H | \psi \rangle$ gives

$$\begin{aligned} \frac{\partial E}{\partial P} &= \left\langle \frac{\partial \psi}{\partial P} \left| \hat{H} \psi \right\rangle + \left\langle \psi \left| \frac{\partial \hat{H}}{\partial P} \psi \right\rangle + \left\langle \psi \left| \hat{H} \frac{\partial \psi}{\partial P} \right\rangle \right. \\ &= E \left(\left\langle \frac{\partial \psi}{\partial P} \left| \psi \right\rangle + \left\langle \psi \left| \frac{\partial \psi}{\partial P} \right\rangle \right) + \left\langle \psi \left| \frac{\partial \hat{H}}{\partial P} \psi \right\rangle = \left\langle \psi \left| \frac{\partial \hat{H}}{\partial P} \psi \right\rangle, \end{aligned} \quad (12.2)$$

because the expression in parentheses is equal to zero (we have profited from the

³We may define $(\frac{\partial \hat{H}}{\partial P})_{P=P_0}$ as an operator, being a limit when $P \rightarrow P_0$ of the operator sequence $\frac{\hat{H}(P) - \hat{H}(P_0)}{P - P_0}$.

facts that the \hat{H} is Hermitian, and that ψ represents its eigenfunction⁴). Indeed, differentiating $\langle\psi|\psi\rangle = 1$ we have:

$$0 = \left\langle \frac{\partial\psi}{\partial P} \middle| \psi \right\rangle + \left\langle \psi \middle| \frac{\partial\psi}{\partial P} \right\rangle, \quad (12.3)$$

which completes the proof.

Soon we will use the Hellmann–Feynman theorem to compute the molecular response to an electric field.⁵

ELECTRIC PHENOMENA

12.2 THE MOLECULE IMMOBILIZED IN AN ELECTRIC FIELD

The electric field intensity \mathcal{E} at a point represents the force acting on a unit positive point charge (probe charge): $\mathcal{E} = -\nabla V$, where V stands for the electric field potential energy at this point.⁶ When the potential changes linearly in space

⁴If, instead of the exact eigenfunction, we use an approximate function ψ , then the theorem would have to be modified. In such a case we have to take into account the terms $\langle \frac{\partial\psi}{\partial P} | \hat{H} | \psi \rangle + \langle \psi | \hat{H} | \frac{\partial\psi}{\partial P} \rangle$.

⁵In case P is a nuclear coordinate (say, x coordinate of the nucleus C , denoted by X_C), and E stands for the potential energy for the motion of the nuclei (cf. Chapter 6, the quantity corresponds to E_0^0 of eq. (6.8)), the quantity $-\frac{\partial E}{\partial P} = F_{X_C}$ represents the x component of the force acting on the nucleus. The Hellmann–Feynman theorem says that this component can be computed as the mean value of the derivative of the Hamiltonian with respect to the parameter P . Since the electronic Hamiltonian reads

$$\begin{aligned} \hat{H}_0 &= -\frac{1}{2} \sum_i \Delta_i + V, \\ V &= -\sum_A \sum_i \frac{Z_A}{r_{Ai}} + \sum_{i < j} \frac{1}{r_{ij}} + \sum_{A < B} \frac{Z_A Z_B}{R_{AB}}, \end{aligned}$$

then, after differentiating, we have as $\frac{\partial \hat{H}}{\partial P}$

$$\frac{\partial \hat{H}_0}{\partial X_C} = \sum_i \frac{Z_C}{(r_{Ci})^3} (X_C - x_i) - \sum_{B(\neq C)} \frac{Z_C Z_B}{(R_{BC})^3} (X_C - X_B).$$

Therefore,

$$F_{X_C} = -\left\langle \psi \middle| \frac{\partial \hat{H}}{\partial P} \middle| \psi \right\rangle = Z_C \left[\int dV_1 \rho(1) \frac{x_1 - X_C}{(r_{C1})^3} - \sum_{B(\neq C)} \frac{Z_B}{(R_{BC})^3} (X_B - X_C) \right],$$

where $\rho(1)$ stands for the electronic density defined in Chapter 11, eq. (11.1).

The last term can be easily calculated from the positions of the nuclei. The first term requires the calculation of the one-electron integrals. Note, that the resulting formula states that the forces acting on the nuclei follow from the *classical* Coulomb interaction involving the electronic density ρ , even if the electronic density has been (and has to be) computed from quantum mechanics.

⁶We see that two potential functions that differ by a constant will give the same forces, i.e. will describe identical physical phenomena (this is why this constant is arbitrary).

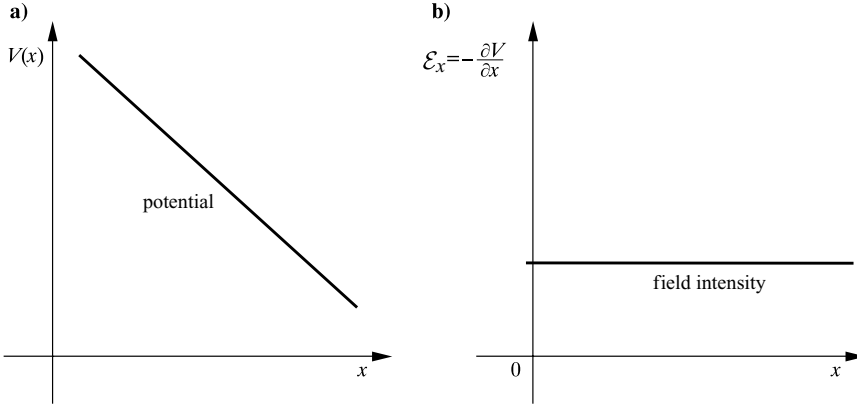


Fig. 12.1. Recalling the electric field properties. (a) 1D: the potential V decreases with x . This means that the electric field intensity \mathcal{E} is constant, i.e. the field is homogeneous (b) 3D; (c) homogeneous electric field $\mathcal{E} = (\mathcal{E}, 0, 0)$; (d) inhomogeneous electric field $\mathcal{E} = (\mathcal{E}(x), 0, 0)$; (e) inhomogeneous electric field $\mathcal{E} = (\mathcal{E}_x(x, y), \mathcal{E}_y(x, y), 0)$.

(Fig. 12.1.a), the electric field intensity is constant (Fig. 12.1.b,c). If at such a potential we shift the probe charge from a to $x + a$, $x > 0$, then the energy will *lower* by $V(x + a) - V(a) = -\mathcal{E}x < 0$. This is similar to the lowering of the potential energy of a stone as it slides downhill.

If, instead of a unit charge, we shift the charge Q , then the energy will change by $-\mathcal{E}Qx$.

It is seen that if we change the *direction* of the shift or the *sign* of the probe charge, then the energy will go *up* (in case of the stone we may change only the direction).

12.2.1 THE ELECTRIC FIELD AS A PERTURBATION

The inhomogeneous field at a slightly shifted point

Imagine a Cartesian coordinate system in 3D space and an inhomogeneous electric field (Fig. 12.1.d,e) in it $\mathcal{E} = [\mathcal{E}_x(x, y, z), \mathcal{E}_y(x, y, z), \mathcal{E}_z(x, y, z)]$.

Assume the electric field vector $\mathcal{E}(\mathbf{r}_0)$ is measured at a point indicated by the vector \mathbf{r}_0 . What will we measure at a point shifted by a small vector $\mathbf{r} = (x, y, z)$ with respect to \mathbf{r}_0 ? The components of the electric field intensity represent smooth functions in space and this is why we may compute the electric field from the Taylor expansion (for each of the components $\mathcal{E}_x, \mathcal{E}_y, \mathcal{E}_z$ separately, all the derivatives are computed at point \mathbf{r}_0):

$$\begin{aligned} \mathcal{E}_x = & \mathcal{E}_{x,0} + \left(\frac{\partial \mathcal{E}_x}{\partial x}\right)_0 x + \left(\frac{\partial \mathcal{E}_x}{\partial y}\right)_0 y + \left(\frac{\partial \mathcal{E}_x}{\partial z}\right)_0 z \\ & + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial x^2}\right)_0 x^2 + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial x \partial y}\right)_0 xy + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial x \partial z}\right)_0 xz \end{aligned}$$

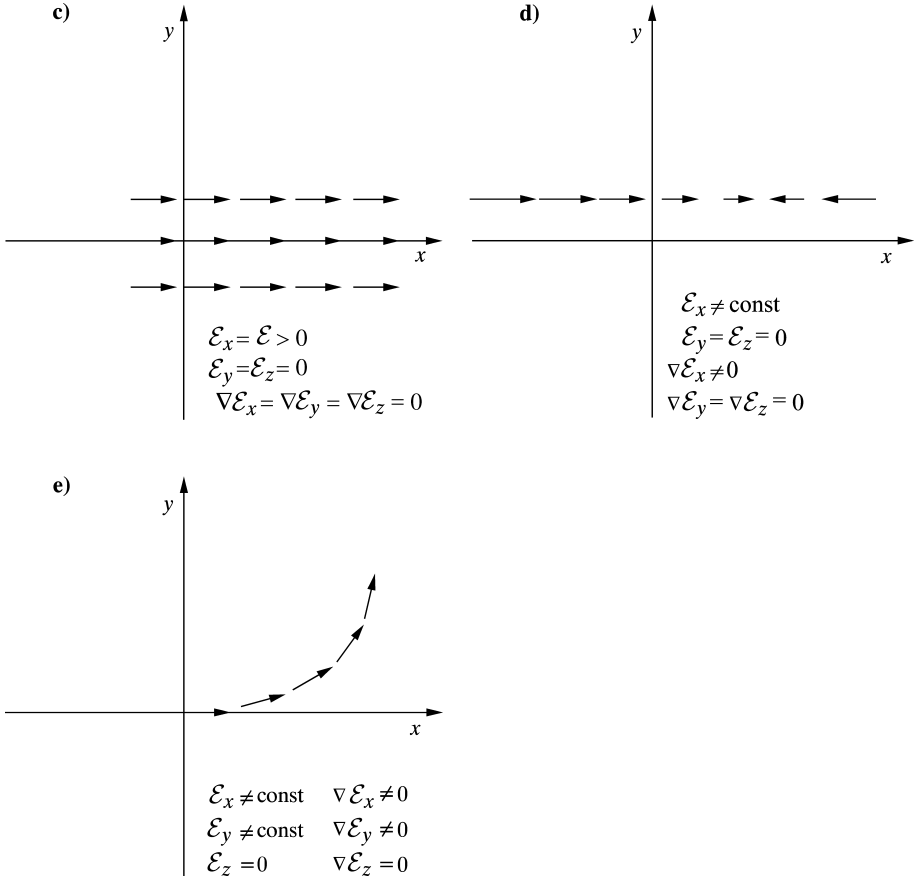


Fig. 12.1. Continued.

$$+ \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial y \partial x} \right)_0 yx + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial y^2} \right)_0 y^2 + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial y \partial z} \right)_0 yz$$

$$+ \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial z \partial x} \right)_0 zx + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial z \partial y} \right)_0 zy + \frac{1}{2} \left(\frac{\partial^2 \mathcal{E}_x}{\partial z^2} \right)_0 z^2 + \dots$$

$\mathcal{E}_y = \dots$ similarly

$\mathcal{E}_z = \dots$ similarly (Fig. 12.2).

Energy gain due to a shift of the electric charge Q

These two electric field intensities (at points \mathbf{r}_0 and $\mathbf{r}_0 + \mathbf{r}$) have been calculated in order to consider the energy gain associated with the shift \mathbf{r} of the electric point charge Q . Similar to the 1D case just considered, we have the energy gain $\Delta E = -Q\mathcal{E} \cdot \mathbf{r}$. There is only one problem: *which* of the two electric field intensities is

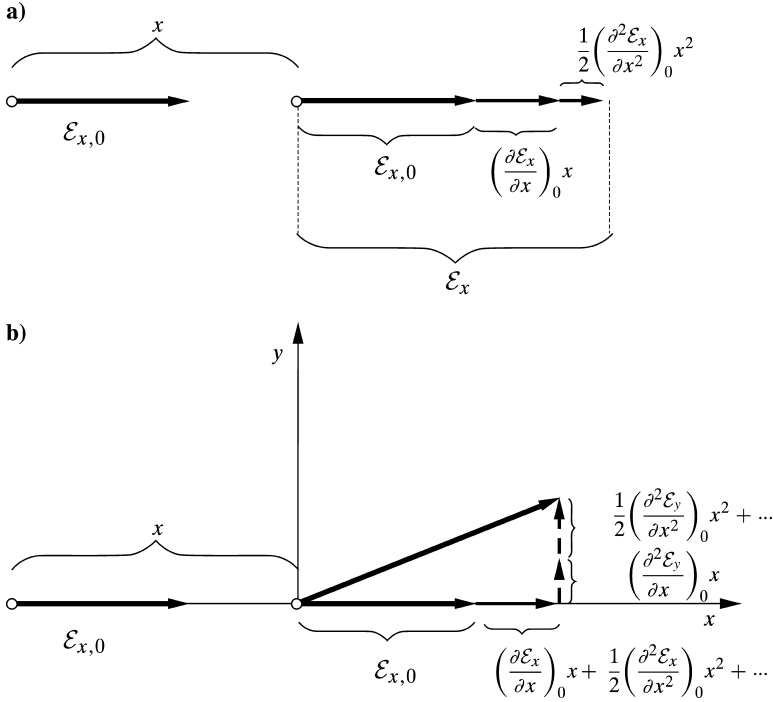


Fig. 12.2. The electric field computed at point $x \ll 1$ from its value (and the values of its derivatives) at point 0. (a) 1D case; (b) 2D case.

to be inserted into the formula? Since the vector $\mathbf{r} = i\mathbf{x} + j\mathbf{y} + k\mathbf{z}$ is small (i, j, k stand for unit vectors corresponding to axes x, y, z , respectively), we may insert, e.g., the mean value of $\mathcal{E}(\mathbf{r}_0)$ and $\mathcal{E}(\mathbf{r}_0 + \mathbf{r})$. We quickly get the following (indices $q, q', q'' \in \{x, y, z\}$):

$$\begin{aligned}
 \Delta E &= -Q\mathcal{E} \cdot \mathbf{r} = -Q\frac{1}{2}[\mathcal{E}(\mathbf{r}_0) + \mathcal{E}(\mathbf{r}_0 + \mathbf{r})]\mathbf{r} \\
 &= -\frac{1}{2}Q[i(\mathcal{E}_{x,0} + \mathcal{E}_x) + j(\mathcal{E}_{y,0} + \mathcal{E}_y) + k(\mathcal{E}_{z,0} + \mathcal{E}_z)](i\mathbf{x} + j\mathbf{y} + k\mathbf{z}) \\
 &= -\mathcal{E}_{x,0}Qx - \mathcal{E}_{y,0}Qy - \mathcal{E}_{z,0}Qz \\
 &\quad - Q\frac{1}{2}\sum_q \left(\frac{\partial \mathcal{E}_x}{\partial q}\right)_0 qx - Q\frac{1}{4}\sum_{q,q'} \left(\frac{\partial^2 \mathcal{E}_x}{\partial q \partial q'}\right)_0 qq'x \\
 &\quad - Q\frac{1}{2}\sum_q \left(\frac{\partial \mathcal{E}_y}{\partial q}\right)_0 qy - Q\frac{1}{4}\sum_{q,q'} \left(\frac{\partial^2 \mathcal{E}_y}{\partial q \partial q'}\right)_0 qq'y \\
 &\quad - Q\frac{1}{2}\sum_q \left(\frac{\partial \mathcal{E}_z}{\partial q}\right)_0 qz - Q\frac{1}{4}\sum_{q,q'} \left(\frac{\partial^2 \mathcal{E}_z}{\partial q \partial q'}\right)_0 qq'z + \dots
 \end{aligned}$$

$$\begin{aligned}
&= -\sum_q \mathcal{E}_{q,0} \tilde{\mu}_q - \frac{1}{2} \sum_{q,q'} \left(\frac{\partial \mathcal{E}_q}{\partial q'} \right)_0 \tilde{\Theta}_{qq'} \\
&\quad - \frac{1}{4} \sum_{q,q',q''} \left(\frac{\partial^2 \mathcal{E}_q}{\partial q' \partial q''} \right)_0 \tilde{\Omega}_{qq'q''} + \dots,
\end{aligned} \tag{12.4}$$

electric
moments

where “+...” denotes higher order terms, while $\tilde{\mu}_q = Qq$, $\tilde{\Theta}_{qq'} = Qqq'$, $\tilde{\Omega}_{qq'q''} = Qqq'q''$, ... represent the components of the successive *moments* of a particle with electric charge Q pointed by the vector $\mathbf{r}_0 + \mathbf{r}$ and calculated within the coordinate system located at \mathbf{r}_0 . For example, $\tilde{\mu}_x = Qx$, $\tilde{\Theta}_{xy} = Qxy$, $\tilde{\Omega}_{xzz} = Qxz^2$, etc.

Traceless multipole moments

The components of such moments in general are not independent. The three components of the dipole moment are indeed independent, but among the quadrupole components we have the obvious relations $\tilde{\Theta}_{qq'} = \tilde{\Theta}_{q'q}$ from their definition, which reduces the number of independent components from 9 to 6. This however is not all. From the Maxwell equations (see Appendix G, p. 962), we obtain the *Laplace equation*, $\Delta V = 0$ (Δ means the Laplacian), valid for points without electric charges. Since $\mathcal{E} = -\nabla V$ and therefore $-\nabla \mathcal{E} = \Delta V$ we obtain

$$\nabla \mathcal{E} = \sum_q \frac{\partial \mathcal{E}_q}{\partial q} = 0. \tag{12.5}$$

Thus, in the energy expression

$$-\frac{1}{2} \sum_{q,q'} \left(\frac{\partial \mathcal{E}_q}{\partial q'} \right)_0 \tilde{\Theta}_{qq'}$$

of eq. (12.4), the quantities $\tilde{\Theta}_{qq'}$ are not independent, since we have to satisfy the condition (12.5).

We have therefore only five independent moments that are quadratic in coordinates. For the same reasons we have only seven (among 27) independent moments with the third power of coordinates. Indeed, ten original components $\Omega_{q,q',q''}$ with $(q, q', q'') = xxx, yxx, yyx, yyy, zxx, zxy, zzx, zyy, zzy, zzz$ correspond to all permutationally non-equivalent moments. We have, however, three relations these components have to satisfy. They correspond to the three equations, each obtained from the differentiation of eq. (12.5) over x, y, z , respectively. This results in only seven *independent* components⁷ $\Omega_{q,q',q''}$.

These relations between moments can be taken into account (adding to the energy expression the zeros resulting from the Laplace equation (12.5)) and we

⁷In Appendix X on p. 1038 the definition of the multipole moments based on polar coordinates is reported. The number of independent components of such moments is equal to the number of independent Cartesian components and equals $(2l+1)$ for $l = 0, 1, 2, \dots$ with the consecutive l pertaining, respectively, to the monopole (or charge) ($2l+1=1$), dipole (3), quadrupole (5), octupole (7), etc. (in agreement with what we find now for the particular moments).

may introduce what are known as the *traceless Cartesian multipole moments*⁸ (the symbol without tilde), which may be chosen in the following way

traceless
moments

$$\mu_q \equiv \tilde{\mu}_q, \quad (12.6)$$

$$\Theta_{qq'} \equiv \frac{1}{2} \left[3\tilde{\Theta}_{qq'} - \delta_{qq'} \sum_q \tilde{\Theta}_{qq} \right]. \quad (12.7)$$

The adjective “traceless” results from relations of the type $\text{Tr } \Theta = \sum_q \Theta_{qq} = 0$, etc.

Then, the expression for the energy contribution changes to (please check that both expressions are identical after using the Laplace formula)

$$\Delta E = - \sum_q \mathcal{E}_{q,0} \mu_q - \frac{1}{3} \sum_{q,q'} \left(\frac{\partial \mathcal{E}_q}{\partial q'} \right)_0 \Theta_{qq'} - \dots \quad (12.8)$$

Most often we compute first the moments and then use them to calculate the traceless multipole moments (cf. Table 9.1 on p. 484).

System of charges in an inhomogeneous electric field

Since we are interested in constructing the *perturbation operator* that is to be added to the Hamiltonian, from now on, according to the postulates of quantum mechanics (Chapter 1), we will treat the coordinates x, y, z in eq. (12.8) as *operators* of multiplication (by just x, y, z). In addition we would like to treat many charged particles, not just one, because we want to consider molecules. To this end we will sum up all the above expressions, computed for each charged particle, separately. As a result the Hamiltonian for the total system (nuclei and electrons) in the electric field \mathcal{E} represents the Hamiltonian of the system without field ($\hat{H}^{(0)}$) and the perturbation ($\hat{H}^{(1)}$):

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)}, \quad (12.9)$$

where

$$\hat{H}^{(1)} = - \sum_q \hat{\mu}_q \mathcal{E}_q - \frac{1}{3} \sum_{qq'} \hat{\Theta}_{qq'} \mathcal{E}_{qq'} \dots \quad (12.10)$$

with the convention

$$\mathcal{E}_{qq'} \equiv \frac{\partial \mathcal{E}_q}{\partial q'},$$

where the field component and its derivatives are computed at a given point (\mathbf{r}_0), e.g., at the centre of mass of the molecule, while $\hat{\mu}_q, \hat{\Theta}_{qq'}, \dots$ denote the operators of the components of the traceless Cartesian multipole moments of the total system, i.e. of the molecule.⁹ How can we imagine multipole moments? We may

⁸The reader will find the corresponding formulae in the article by A.D. Buckingham, *Advan. Chem. Phys.* 12 (1967) 107 or by A.J. Sadlej, “*Introduction to the Theory of Intermolecular Interactions*”, Lund’s Theoretical Chemistry Lecture Notes, Lund, 1990.

⁹Also calculated with respect to this point. This means that if the molecule is large, then \mathbf{r} may become dangerously large. In such a case, as a consequence, the series (12.8) may converge slowly.

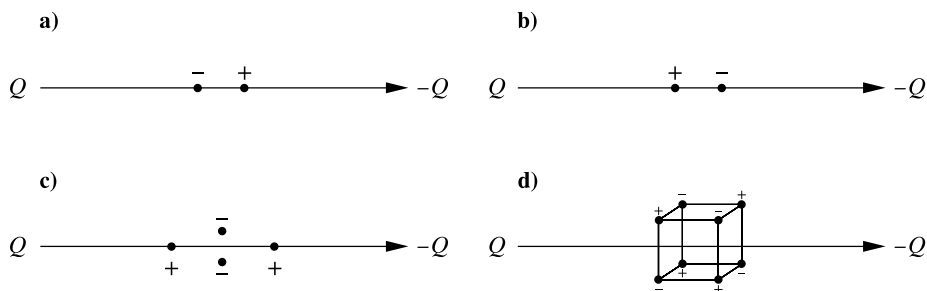


Fig. 12.3. Explanation of why a dipole moment interacts with the electric field intensity, a quadrupole moment with its gradient, while the octupole moment does not interact either with the first or with the second. The external electric field is produced by two *distant* electric charges $Q > 0$ and $-Q$ (for long distances between them the field in the central region between the charges resembles a homogeneous field) and interacts with an object (a dipole, a quadrupole, etc.) located in the central region. A favourable orientation of the object corresponds to the lowest interaction energy with Q and $-Q$. Fig. (a) shows such a low-energy situation for a dipole: the charge “+” protrudes towards $-Q$, while the charge “-” protrudes towards Q . Fig. (b) corresponds to the opposite situation, energetically non-favourable. As we can see, the interaction energy of the dipole with the electric field *differentiates* these two situations. Now, let us locate a quadrupole in the middle (c). Let us imagine that a neutral point object has just split into four point charges (of the same absolute value). The system lowers its energy by the “-” charges going off the axis, because they have increased their distance from the charge $-Q$, but at the same time the system energy has increased by the same amount, since the charges went off the symmetrically located charge $+Q$. What about the “+” charges? The splitting of the “++” charges leads to an energy gain for the right-hand side “+” charge, because it approached $-Q$, and went off the charge $+Q$, but the left-hand side “+” charge gives the opposite energy effect. Altogether the net result is zero. Conclusion: *the quadrupole does not interact with the homogeneous electric field*. Now, let us imagine an inhomogeneous field having a non-zero gradient along the axis (e.g., both Q charges differ by their absolute values). There will be no energy difference for the minus charges, but one of the plus charges will be attracted more strongly than the other. Therefore, *the quadrupole interacts with the field gradient*. We may foresee that the quadrupole will align with its longer axis along the field. Fig. (d) shows an octupole (all charges have the same absolute value). Indeed, the total charge, all the components of the dipole as well as of quadrupole moment are equal to zero, but the octupole (eight charges in the vertices of a cube) is non-zero. Such an octupole does not interact with a homogeneous electric field (because the right and left sides of the cube do not gain anything when interacting). It also does not interact with the field gradient (because each of the above mentioned sides of the cube is composed of two plus and two minus charges; what the first ones gain the second ones lose).

associate a given multipole moment with a simple object that exhibits a non-zero value for this particular moment, but all lower multipole moments equal zero.¹⁰ Some of such objects are shown in Fig. 12.3, located between two charges Q and $-Q$ producing an “external field”. Note that the multipole moment names (*dipole*, *quadrupole*, *octupole*) indicate the *number* of the point charges from which these objects are built.

Eq. (12.10) means that if the system exhibits non-zero multipole moments (before any interaction or due to the interaction), they will interact with the external electric field: the dipole with the electric field intensity, the quadrupole with its gradient, etc. Fig. 12.3 shows why this happens.

¹⁰Higher moments in general will be non-zero.

12.2.2 THE HOMOGENEOUS ELECTRIC FIELD

In case of a *homogeneous* external electric field, the contribution to $\hat{H}^{(1)}$ comes from the first term in eq. (12.10):

$$\hat{H} = \hat{H}^{(0)} + \hat{H}^{(1)} = \hat{H}^{(0)} - \hat{\mu}_x \mathcal{E}_x - \hat{\mu}_y \mathcal{E}_y - \hat{\mu}_z \mathcal{E}_z = \hat{H}^{(0)} - \hat{\boldsymbol{\mu}} \cdot \boldsymbol{\mathcal{E}}, \quad (12.11)$$

where the dipole moment operator $\hat{\boldsymbol{\mu}}$ has the form:

$$\hat{\boldsymbol{\mu}} = \sum_i \mathbf{r}_i Q_i, \quad (12.12)$$

with the vector \mathbf{r}_i indicating the particle i of charge Q_i .

Hence,

$$\frac{\partial \hat{H}}{\partial \mathcal{E}_q} = -\hat{\mu}_q. \quad (12.13)$$

From this it follows

$$\left\langle \psi \left| \frac{\partial \hat{H}}{\partial \mathcal{E}_q} \psi \right. \right\rangle = -\langle \psi | \hat{\mu}_q | \psi \rangle = -\mu_q, \quad (12.14)$$

where μ_q is the expected value of the q -th component of the dipole moment.

From the Hellmann–Feynman theorem we have:

$$\left\langle \psi \left| \frac{\partial \hat{H}}{\partial \mathcal{E}_q} \psi \right. \right\rangle = \frac{\partial E}{\partial \mathcal{E}_q}, \quad (12.15)$$

therefore

$$\frac{\partial E}{\partial \mathcal{E}_q} = -\mu_q. \quad (12.16)$$

On the other hand, in the case of a *weak electric field* $\boldsymbol{\mathcal{E}}$ we certainly may write the Taylor expansion:

$$\begin{aligned} E(\boldsymbol{\mathcal{E}}) &= E^{(0)} + \sum_q \left(\frac{\partial E}{\partial \mathcal{E}_q} \right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_q + \frac{1}{2!} \sum_{q,q'} \left(\frac{\partial^2 E}{\partial \mathcal{E}_q \partial \mathcal{E}_{q'}} \right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_q \mathcal{E}_{q'} \\ &+ \frac{1}{3!} \sum_{q,q',q''} \left(\frac{\partial^3 E}{\partial \mathcal{E}_q \partial \mathcal{E}_{q'} \partial \mathcal{E}_{q''}} \right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} + \dots, \end{aligned} \quad (12.17)$$

where $E^{(0)}$ stands for the energy of the unperturbed molecule.

Linear and non-linear responses to a homogeneous electric field

Comparing (12.16) and (12.17) we get,

$$\begin{aligned} \frac{\partial E}{\partial \mathcal{E}_q} &= -\mu_q = \left(\frac{\partial E}{\partial \mathcal{E}_q} \right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} + \sum_{q'} \left(\frac{\partial^2 E}{\partial \mathcal{E}_q \partial \mathcal{E}_{q'}} \right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_{q'} \\ &+ \frac{1}{2} \sum_{q',q''} \left(\frac{\partial^3 E}{\partial \mathcal{E}_q \partial \mathcal{E}_{q'} \partial \mathcal{E}_{q''}} \right)_{\boldsymbol{\mathcal{E}}=\mathbf{0}} \mathcal{E}_{q'} \mathcal{E}_{q''} \dots, \end{aligned} \quad (12.18)$$

induced dipole
moment

or replacing the derivatives by their equivalents (permanent dipole moment, molecular polarizability and hyperpolarizabilities)

$$\mu_q = \mu_{0q} + \sum_{q'} \alpha_{qq'} \mathcal{E}_{q'} + \frac{1}{2} \sum_{q'q''} \beta_{qq'q''} \mathcal{E}_{q'} \mathcal{E}_{q''} + \dots \quad (12.19)$$

dipole
polarizability

The meaning of the formula for μ_q is clear: in addition to the permanent dipole moment μ_0 of the isolated molecule, we have its modification, i.e. an induced dipole moment, which consists of the *linear* part in the field ($\sum_{q'} \alpha_{qq'} \mathcal{E}_{q'}$) and of the *nonlinear* part ($\frac{1}{2} \sum_{q'q''} \beta_{qq'q''} \mathcal{E}_{q'} \mathcal{E}_{q''} + \dots$). The quantities that characterize the molecule: vector μ_0 and tensors α, β, \dots are of key importance. By comparing (12.18) with (12.19) we have the following relations:

the permanent (field-independent) dipole moment of the molecule (component q):

$$\mu_{0q} = - \left(\frac{\partial E}{\partial \mathcal{E}_q} \right)_{\mathcal{E}=0}, \quad (12.20)$$

the total dipole moment (field-dependent):

$$\mu_q = - \left(\frac{\partial E}{\partial \mathcal{E}_q} \right), \quad (12.21)$$

the component qq' of the dipole polarizability tensor:

$$\alpha_{qq'} = - \left(\frac{\partial^2 E}{\partial \mathcal{E}_q \partial \mathcal{E}_{q'}} \right)_{\mathcal{E}=0} = \left(\frac{\partial \mu_q}{\partial \mathcal{E}_{q'}} \right)_{\mathcal{E}=0}, \quad (12.22)$$

the component $qq'q''$ of the dipole hyperpolarizability tensor:

$$\beta_{qq'q''} = - \left(\frac{\partial^3 E}{\partial \mathcal{E}_q \partial \mathcal{E}_{q'} \partial \mathcal{E}_{q''}} \right)_{\mathcal{E}=0}. \quad (12.23)$$

dipole hyper-
polarizabilities

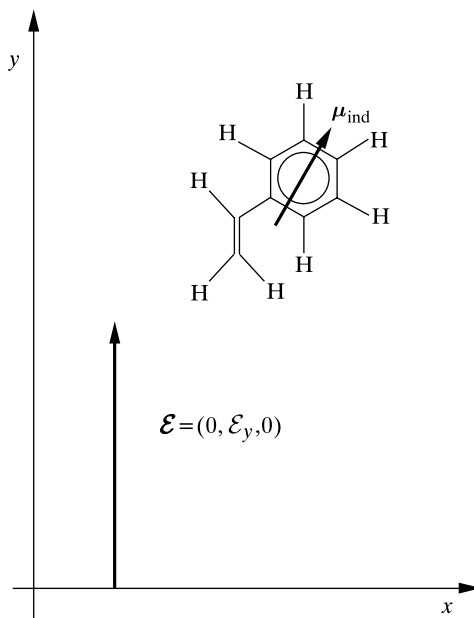
Next, we obtain higher-order dipole hyperpolarizabilities (γ, \dots), which will contribute to the characteristics of the way the molecule is polarized when subject to a weak electric field.

The homogeneous field: dipole polarizability and dipole hyperpolarizabilities

From eq. (12.17) we have the following expression for the energy of the molecule in the electric field

$$\begin{aligned} E(\mathcal{E}) = E^{(0)} - \sum_q \mu_{0q} \mathcal{E}_q - \frac{1}{2} \sum_{qq'} \alpha_{qq'} \mathcal{E}_q \mathcal{E}_{q'} - \frac{1}{3!} \sum_{qq'q''} \beta_{qq'q''} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} \\ - \frac{1}{4!} \sum_{qq'q''q'''} \gamma_{qq'q''q'''} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} \mathcal{E}_{q'''} \dots \end{aligned} \quad (12.24)$$

Fig. 12.4. The direction of the induced dipole moment may differ from the direction of the electric field applied (due to the tensor character of the polarizability and hyperpolarizabilities). Example: the vinyl molecule in a planar conformation. Assume the following Cartesian coordinate system: x (horizontal in the figure plane), y (vertical in the figure plane) and z (perpendicular to the figure plane), and the external electric field: $\mathcal{E} = (0, \mathcal{E}_y, 0)$. The component x of the induced dipole moment is equal to (within the accuracy of linear terms, eq. (12.19)) $\mu_{\text{ind},x} = \mu_x - \mu_{0x} \approx \alpha_{xy}\mathcal{E}_y$, $\mu_{\text{ind},y} \approx \alpha_{yy}\mathcal{E}_y$, $\mu_{\text{ind},z} \approx \alpha_{zy}\mathcal{E}_y$. Due to the symmetry plane $z = 0$ of the molecule (cf. p. 630) $\alpha_{zy} = \alpha_{zx} = 0$, and similarly for the hyperpolarizabilities, we have $\mu_{\text{ind},z} = 0$. As we can see, despite the field having its x component equal to zero, the induced dipole moment x component does not ($\mu_{\text{ind},x} \neq 0$).



This formula pertains exclusively to the interaction of the molecular *dipole* (the permanent dipole plus the induced linear and non-linear response) with the electric field. As seen from (12.19), the induced dipole moment with the components $\mu_q - \mu_{0q}$ may have a different direction from the applied electric field (due to the tensor character of the polarizability and hyperpolarizabilities). This is quite understandable, because the electrons will move in a direction which will represent a compromise between the direction of the electric field which forces them to move, and the direction where the polarization of the molecule is easiest (Fig. 12.4).

It is seen from eqs. (12.19) and (12.22) that:

- As a second derivative of a continuous function E the polarizability represents a symmetric tensor ($\alpha_{qq'} = \alpha_{q'q}$).
- The polarizability characterizes this part of the *induced dipole moment, which is proportional to the field*.
- If non-diagonal components of the polarizability tensor are non-zero, then the flow direction of the charge within the molecule will differ from the direction of the field. This would happen when the electric field forced the electrons to flow into empty space, while they had a “highway” to travel along some chemical bonds (cf. Fig. 12.4).
- If a molecule is symmetric with respect to the plane $q = 0$, say, $z = 0$, then all the (hyper)polarizabilities with odd numbers of the indices z , are equal to zero (cf. Fig. 12.4). It has to be like this, because otherwise a change of the electric field component from \mathcal{E}_z to $-\mathcal{E}_z$ would cause a change in energy (see eq. (12.24)), which is impossible, because the molecule is symmetric with respect to the plane $z = 0$.

- The dipole *hyperpolarizabilities* (β and higher-order) are very important, because, if we limited ourselves to the first two terms of (12.19) containing only μ_{0q} and $\alpha_{qq'}$ (i.e. neglecting β and higher hyperpolarizabilities), the molecule would be equally easy to polarize in two opposite directions.¹¹ This is why, for a molecule with a centre of inversion, all *odd* dipole hyperpolarizabilities (i.e. with an odd number of indices q) have to equal zero, because the invariance of the energy with respect to the inversion will be preserved that way. If the molecule does not exhibit an inversion centre, the non-zero odd dipole hyperpolarizabilities ensure that polarization of the molecule depends, in general, on whether we change the electric field vector to the opposite direction. This is how it should be. Why were the electrons able to move to the same extent towards an electron donor (on one end of the molecule) as to an electron acceptor (on the other end)?

Does the dipole moment really exist?

Now, let us complicate things. What is μ_0 ? We used to say that it is the dipole moment of the molecule in its ground state. Unfortunately, no molecule has a non-zero dipole moment. This follows from the invariance of the Hamiltonian with respect to the inversion operation and was described on p. 65. The mean value of the dipole moment operator is bound to be zero since the square of the wave function is symmetric, while the dipole moment operator itself is antisymmetric with respect to the inversion. Thus for *any* molecule¹² $\mu_{0q} = 0$ for $q = x, y, z$. The reason is the rotational part of the wave function (cf. p. 230). This is quite natural. Dear reader, did you ever think why the hydrogen atom does not exhibit a dipole moment despite having two poles: the proton and the electron? The reason is the same. The electron in its ground state is described by the 1s orbital, which does not prefer any direction and the dipole moment integral for the hydrogen atom gives zero. Evidently, we have got into trouble.

The trouble disappears after the Born–Oppenheimer approximation (the clamped nuclei approximation, cf. p. 227) is used, i.e. if we hold the *molecule fixed in space*. In such a case, the molecule *has* the dipole moment and this dipole moment is to be inserted into formulae as μ_0 , and then we may calculate the polarizability, hyperpolarizabilities, etc. But what do we do, when we do not apply the Born–Oppenheimer approximation? Yet, in experiments we do not use the Born–Oppenheimer approximation (or any other). We have to allow the molecule to rotate and then the dipole moment μ_0 disappears.

It is always good to see things working in a simple model, and simple models resulting in exact solutions of the Schrödinger equation have been described in

¹¹According to eq. (12.19) the absolute value of the q component of the *induced dipole moment* $\mu_{\text{ind}} = \mu - \mu_0$ would be identical for \mathcal{E}_q as well as for $-\mathcal{E}_q$.

¹²“Everybody knows” that the HF molecule has a non-zero dipole moment. Common knowledge says that when an electric field is applied, the HF dipole aligns itself along the electric field vector. At any field, no matter how small? This would be an incredible scenario. No, the picture has to be more complex.

Chapter 4. A good model for our rotating molecule may be the rigid rotator with a dipole moment (a charge Q on one mass and $-Q$ on the other).¹³ The Hamiltonian remains, in principle, the same as for the rigid rotator, because we have to add a *constant* $-\frac{Q^2}{R}$ to the potential energy, which does not change anything. Thus the ground state wave function is Y_0^0 as before, which tells us that *every* orientation of the rigid dipolar rotor in space is *equally probable*.

Well, what if the rotating molecule is located in a *very weak* electric field? After the field is switched on the molecule will of course continue to rotate, but a tiny preference of those orientations which orient the dipole at least partly *along* the electric field, will appear. We may say that the system will have a certain *polarizability*, which can be computed as a negative second derivative of the energy with respect to the electric field. This effect will be described by our perturbation theory, eq. (12.22). If the electric field were of medium intensity, instead of the orientational preferences, the rotator would already pay great attention to it, and would “oscillate” about the direction of the electric field \mathcal{E} . This would already be beyond the capabilities of perturbation theory (too large perturbation). Finally, if the electric field were very strong (e.g., along the x axis), the rotator would orient *exactly along the field*, the energy gain would be equal to¹⁴ $-\boldsymbol{\mu} \cdot \mathcal{E} = -QRE_x$ and its second derivative would be zero (as well as the polarizability).¹⁵ Therefore,¹⁶

¹³This moment therefore has a constant length.

¹⁴This is what we often assume in phenomenological theories, forgetting that at weak field intensities the situation is different.

¹⁵The case we have been talking about pertains to the ground state of the system. What if the electric field were applied to the system in its excited state? For a medium electric field, the subsequent energy levels as functions of the field will be nearly equidistant. Why? The reason is quite simple. For medium electric fields the eigenstates of the rotator will be related to its *oscillations* about the direction of the field. In the harmonic approximation this means equidistant energy eigenvalues. The corresponding vibrational wave functions (that depend on the deviation angle θ from the direction of the field) will have large amplitudes for small θ values and an increasing number of nodes when the vibrational quantum number increases.

¹⁶A detailed analysis of this problem was carried out by Grzegorz Łach (these results prior to publication are acknowledged). Two asymptotic dependencies of energy as a function of electric field intensity have been obtained: $E(\mathcal{E}) = \frac{1}{I} f(I\mu\mathcal{E})$, where I stands for the moment of the inertia of the rotator, and the function $f(x)$ for small field intensities (this results from a perturbation theory with the unperturbed system corresponding to the absence of an electric field)

$$f(x) = -\frac{1}{3}x^2 + \frac{11}{135}x^4 - \frac{376}{8505}x^6 + \dots$$

for very large field intensities

$$f(x) = -x + \sqrt{x} - \frac{1}{4} - \frac{1}{64} \frac{1}{\sqrt{x}} + \dots$$

It has been shown, that the first two terms in the last formula also follow from perturbation theory. However, in this perturbation theory the unperturbed operator does not correspond to the free molecule, but in addition contains a harmonic oscillator potential (with the angle θ as the corresponding coordinate). The anharmonicity is treated as a perturbation.

at weak electric fields we expect quadratic dependence of the energy on the field and only at stronger fields may we expect linear dependence.

12.2.3 THE INHOMOGENEOUS ELECTRIC FIELD: MULTIPOLE POLARIZABILITIES AND HYPERPOLARIZABILITIES

dipole
polarizabilities
and hyper-
polarizabilities

The formula $\mu_q = \mu_{0q} + \sum_{q'} \alpha_{qq'} \mathcal{E}_{q'} + \frac{1}{2} \sum_{q', q''} \beta_{qq'q''} \mathcal{E}_{q'} \mathcal{E}_{q''} + \dots$ pertains to the polarizabilities and hyperpolarizabilities in a *homogeneous* electric field. The polarizability $\alpha_{qq'}$ characterizes a *linear* response of the molecular *dipole* moment to the electric field, the hyperpolarizability $\beta_{qq'q''}$ and the higher ones characterize the corresponding *non-linear* response of the molecular *dipole* moment. However, a change of the charge distribution contains more information than just that offered by the induced dipole moment. For a *non-homogeneous* electric field the energy expression changes, because besides the dipole moment, higher multipole moments (permanent as well as induced) come into play (see Fig. 12.3). Using the Hamiltonian (12.9) with the perturbation (12.10) (which corresponds to a molecule immersed in a non-homogeneous electric field) we obtain the following energy expression from the Hellmann–Feynman theorem (formula (12.15)) and eq. (12.17):

$$E(\mathcal{E}) = E^{(0)} + E_\mu + E_\Theta + E_{\mu-\Theta} + \dots, \quad (12.25)$$

where besides the unperturbed energy $E^{(0)}$, we have:

- the dipole–field interaction energy E_μ (including the permanent and induced dipole – these terms appeared earlier for the homogeneous field):

$$E_\mu = - \left[\sum_q \mu_{0q} \mathcal{E}_q + \frac{1}{2} \sum_{qq'} \alpha_{qq'} \mathcal{E}_q \mathcal{E}_{q'} + \frac{1}{6} \sum_{q, q', q''} \beta_{qq', q''} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} \dots \right], \quad (12.26)$$

- next, the terms that pertain to the *inhomogeneity* of the electric field: the energy E_Θ of the interaction of the field gradient with the quadrupole moment (the permanent one Θ – the first term, and of the induced one; C stands for the *quadrupole polarizability*, and then, in the terms denoted by “+ ...” there are the non-linear responses with *quadrupole hyperpolarizabilities*):

quadrupole
polarizability

$$E_\Theta = - \left[\frac{1}{3} \sum_{qq'} \Theta_{qq'} \mathcal{E}_{qq'} + \frac{1}{6} \sum_{qq', q'', q'''} C_{qq', q'', q'''} \mathcal{E}_{qq'} \mathcal{E}_{q''} \mathcal{E}_{q'''} + \dots \right], \quad (12.27)$$

- the dipole–quadrupole cross term $E_{\mu-\Theta}$:

$$E_{\mu-\Theta} = - \left[\frac{1}{3} \sum_{q, q', q''} A_{q, q', q''} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} + \frac{1}{6} \sum_{q, q', q'', q'''} B_{qq', q'', q'''} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} \mathcal{E}_{q'''} \right] \quad (12.28)$$

and

- the interaction of higher multipoles (permanent as well as induced: first, the octupole Ω with the corresponding *octupole polarizabilities and hyperpolarizabilities*, etc.) with the higher derivatives of electric field together with the corresponding cross terms denoted as: $+\dots$.

octupole
polarizability

12.3 HOW TO CALCULATE THE DIPOLE MOMENT

The dipole moment in the normalized state $|n\rangle$ is calculated (according to the postulates of quantum mechanics, Chapter 1) as the mean value $\boldsymbol{\mu} = \langle n | \hat{\boldsymbol{\mu}} | n \rangle$ of the dipole moment operator¹⁷

$$\hat{\boldsymbol{\mu}} = - \sum_i \mathbf{r}_i + \sum_A Z_A \mathbf{R}_A, \quad (12.29)$$

where \mathbf{r}_i are the vectors indicating the electrons and \mathbf{R}_A shows nucleus A with the charge Z_A (in a.u.).

For a neutral molecule only, the dipole moment operator and the dipole moment itself do not depend on the choice of the origin of the coordinate system. When two coordinate systems differ by translation \mathbf{R} , then, in general, we may obtain two different results (\mathbf{r}_i and Q_i stand for the position vector and charge of particle i):

$$\begin{aligned} \hat{\boldsymbol{\mu}} &= \sum_i Q_i \mathbf{r}_i, \\ \hat{\boldsymbol{\mu}}' &= \sum_i Q_i \mathbf{r}'_i = \sum_i Q_i (\mathbf{r}_i + \mathbf{R}) = \hat{\boldsymbol{\mu}} + \sum_i Q_i \mathbf{R} = \hat{\boldsymbol{\mu}} + \mathbf{R} \sum_i Q_i. \end{aligned} \quad (12.30)$$

It is seen that $\hat{\boldsymbol{\mu}}' = \hat{\boldsymbol{\mu}}$, only if $\sum_i Q_i = 0$, i.e. for a neutral system.¹⁸

This represents a special case of the theorem, saying that the lowest non-vanishing multipole moment does not depend on the choice of the coordinate system; all others may depend on that choice.

12.3.1 HARTREE-FOCK APPROXIMATION

In order to show the reader how we calculate the dipole moment in practice, let us use the Hartree–Fock approximation. Using the normalized Slater determinant $|\Phi_0\rangle$ we have as the Hartree–Fock approximation to the dipole moment:

$$\begin{aligned} \boldsymbol{\mu} &= \langle \Phi_0 | - \sum_i \mathbf{r}_i + \sum_A Z_A \mathbf{R}_A | \Phi_0 \rangle = \langle \Phi_0 | - \sum_i \mathbf{r}_i | \Phi_0 \rangle + \langle \Phi_0 | \sum_A Z_A \mathbf{R}_A | \Phi_0 \rangle \\ &= \boldsymbol{\mu}_{\text{el}} + \boldsymbol{\mu}_{\text{nucl}}, \end{aligned} \quad (12.31)$$

where the integration goes over the electronic coordinates. The dipole moment of the nuclei $\boldsymbol{\mu}_{\text{nucl}} = \sum_A Z_A \mathbf{R}_A$ is very easy to compute, because, in the Born–

¹⁷As is seen, this is an operator having x , y and z components in a chosen coordinate system and each of its components means a *multiplication by the corresponding coordinates and electric charges*.

¹⁸If you ever have to debug a computer program that calculates the dipole moment, then please remember there is a simple and elegant test at your disposal that is based on the above theorem. You just make two runs of the program for a neutral system each time using a different coordinate system (the two systems differing by a translation). The two results have to be identical.

Oppenheimer approximation, the nuclei occupy some fixed positions in space. The electronic component of the dipole moment $\mu_{\text{el}} = \langle \Phi_0 | - \sum_i \mathbf{r}_i | \Phi_0 \rangle$, according to the Slater–Condon rules (Appendix M on p. 986), amounts to: $\mu_{\text{el}} = - \sum_i n_i \langle \varphi_i | \mathbf{r}_i | \varphi_i \rangle$, where n_i stands for the occupation number of the orbital φ_i (let us assume double occupation, i.e. $n_i = 2$). After the LCAO expansion is applied $\varphi_i = \sum_j c_{ji} \chi_j$ and combining the coefficients c_{ji} into the bond order matrix (see p. 365) \mathbf{P} , we have

$$\mu_{\text{el}} = - \sum_{kl} P_{lk} (\chi_k | \mathbf{r} | \chi_l). \quad (12.32)$$

This is in principle all we can say about calculation of the dipole moment in the Hartree–Fock approximation. The rest belongs to the technical side. We choose a coordinate system and calculate all the integrals of type $(\chi_k | \mathbf{r} | \chi_l)$, i.e. $(\chi_k | x | \chi_l)$, $(\chi_k | y | \chi_l)$, $(\chi_k | z | \chi_l)$. The bond order matrix \mathbf{P} is just a by-product of the Hartree–Fock procedure.

12.3.2 ATOMIC AND BOND DIPOLES

It is interesting that the total dipole moment can be decomposed into atomic and pairwise contributions:

$$\mu_{\text{el}} = - \sum_A \sum_{k \in A} \sum_{l \in A} P_{lk} (\chi_k | \mathbf{r} | \chi_l) - \sum_A \sum_{k \in A} \sum_{B \neq A} \sum_{l \in B} P_{lk} (\chi_k | \mathbf{r} | \chi_l), \quad (12.33)$$

where we assume that the atomic orbital centres (A, B) correspond to the nuclei. If the two atomic orbitals k and l belong to *the same* atom, then we insert $\mathbf{r} = \mathbf{R}_A + \mathbf{r}_A$, where \mathbf{R}_A indicates the atom (nucleus) A from the origin, and \mathbf{r}_A indicates the separation of the electron from the local origin centred on A . If k and l belong to *different* atoms, then $\mathbf{r} = \mathbf{R}_{AB} + \mathbf{r}_{AB}$, where \mathbf{R}_{AB} indicates the centre of the AB section, and \mathbf{r}_{AB} represents the position of the electron with respect to this centre. Then,

$$\begin{aligned} \mu_{\text{el}} = & - \sum_A \mathbf{R}_A \sum_{k \in A} \sum_{l \in A} S_{kl} P_{lk} - \sum_A \sum_{k \in A} \sum_{l \in A} P_{lk} (\chi_k | \mathbf{r}_A | \chi_l) \\ & - \sum_A \sum_{B \neq A} \mathbf{R}_{AB} \sum_{k \in A} \sum_{l \in B} S_{kl} P_{lk} - \sum_A \sum_{k \in A} \sum_{B \neq A} \sum_{l \in B} P_{lk} (\chi_k | \mathbf{r}_{AB} | \chi_l), \end{aligned} \quad (12.34)$$

where S_{kl} are the overlap integrals. After adding the dipole moment of the nuclei we obtain

$$\mu = \sum_A \mu_A + \sum_A \sum_{B \neq A} \mu_{AB}, \quad (12.35)$$

where

$$\begin{aligned} \mu_A = & \mathbf{R}_A \left(Z_A - \sum_{k \in A} \sum_{l \in A} S_{kl} P_{lk} \right) - \sum_A \sum_{k \in A} \sum_{l \in A} P_{lk} (\chi_k | \mathbf{r}_A | \chi_l) \\ \mu_{AB} = & - \sum_A \sum_{B \neq A} \mathbf{R}_{AB} \sum_{k \in A} \sum_{l \in B} S_{kl} P_{lk} - \sum_A \sum_{k \in A} \sum_{B \neq A} \sum_{l \in B} P_{lk} (\chi_k | \mathbf{r}_{AB} | \chi_l). \end{aligned}$$

We therefore have a quite interesting result:¹⁹

The molecular dipole moment can be represented as the sum of the individual atomic dipole moments and the pairwise atomic dipole contributions.

The P_{lk} is large, when k and l belong to the atoms forming the *chemical bonds* (if compared to two non-bonded atoms, see Appendix S, p. 1015), therefore the dipole moments related to *pairs* of atoms come practically uniquely from *chemical bonds*. The contribution of the lone pairs of the atom A is hidden in the second term of μ_A and may be quite large (cf. Appendix T on p. 1020).

12.3.3 WITHIN THE ZDO APPROXIMATION

In several semiempirical methods of quantum chemistry (e.g., in the Hückel method) we assume the Zero Differential Overlap (ZDO) approximation, i.e. that $\chi_k \chi_l \approx (\chi_k)^2 \delta_{kl}$ and hence the second terms in μ_A as well as in μ_{AB} are equal to zero,²⁰ and therefore

$$\mu = \sum_A R_A \left(Z_A - \sum_{k \in A} P_{kk} \right) = \sum_A R_A Q_A, \quad (12.36)$$

where $Q_A = (Z_A - \sum_{k \in A} P_{kk})$ represents the net electric charge of the atom A . This result is extremely simple: the dipole moment comes from the atomic charges only.

12.4 HOW TO CALCULATE THE DIPOLE POLARIZABILITY

12.4.1 SUM OVER STATES METHOD (SOS)

Perturbation theory gives the energy of the ground state $|0\rangle$ in a weak electric field as (the sum of the zeroth, first and second-order energies,²¹ eqs. (5.22) and (5.26)):

$$E(\mathcal{E}) = E^{(0)} + \langle 0 | \hat{H}^{(1)} | 0 \rangle + \sum_n' \frac{|\langle 0 | \hat{H}^{(1)} | n \rangle|^2}{E_0^{(0)} - E_n^{(0)}} + \dots \quad (12.37)$$

If we assume a homogeneous electric field (see eq. (12.11)), the perturbation is equal to $\hat{H}^{(1)} = -\hat{\mu} \cdot \mathcal{E}$, and we obtain

$$E = E^{(0)} - \langle 0 | \hat{\mu} | 0 \rangle \cdot \mathcal{E} + \sum_n' \frac{[\langle 0 | \hat{\mu} | n \rangle \cdot \mathcal{E}][\langle n | \hat{\mu} | 0 \rangle \cdot \mathcal{E}]}{E_0^{(0)} - E_n^{(0)}} + \dots \quad (12.38)$$

The first term represents the energy of the unperturbed molecule, the second term is a correction for the interaction of the permanent dipole moment with the field.

¹⁹This does not represent a unique partitioning, only the total dipole moment should remain the same. For example, the individual atomic contributions include the lone pairs, which otherwise could be counted as a separate lone pair contribution.

²⁰The second term in μ_A is equal to zero, because the integrands $\chi_k^2 x$, $\chi_k^2 y$, $\chi_k^2 z$ are all antisymmetric with respect to transformation of the coordinate system $x \rightarrow -x$, $y \rightarrow -y$, $z \rightarrow -z$.

²¹Prime in the summation means that the m -th state is excluded.

The next term already takes into account that the *induced moment* also interacts with the electric field (eq. (12.19)):

$$\sum_n' \frac{[\langle 0|\hat{\boldsymbol{\mu}}|n\rangle \cdot \boldsymbol{\mathcal{E}}][\langle n|\hat{\boldsymbol{\mu}}|0\rangle \cdot \boldsymbol{\mathcal{E}}]}{E^{(0)} - E_n^{(0)}} = -\frac{1}{2} \sum_{qq'} \alpha_{qq'} \mathcal{E}_q \mathcal{E}_{q'}, \quad (12.39)$$

where the component qq' of the polarizability is equal to

$$\alpha_{qq'} = 2 \sum_n' \frac{\langle 0|\hat{\boldsymbol{\mu}}_q|n\rangle \langle n|\hat{\boldsymbol{\mu}}_{q'}|0\rangle}{\Delta_n}, \quad (12.40)$$

where $\Delta_n = E_n^{(0)} - E^{(0)}$. The polarizability has the dimension of volume.²²

Similarly, we may obtain the perturbational expressions for the dipole, quadrupole, octupole hyperpolarizabilities, etc. For example, the ground-state dipole hyperpolarizability β_0 has the form (the $qq'q''$ component, where the prime means that the ground state is omitted – we skip the derivation):

$$\beta_{qq'q''} = \sum_{n,m}' \frac{\langle 0|\hat{\boldsymbol{\mu}}_q|n\rangle \langle n|\hat{\boldsymbol{\mu}}_{q'}|m\rangle \langle m|\hat{\boldsymbol{\mu}}_{q''}|0\rangle}{\Delta_n \Delta_m} - \langle 0|\hat{\boldsymbol{\mu}}_q|0\rangle \sum_n' \frac{\langle 0|\hat{\boldsymbol{\mu}}_{q'}|n\rangle \langle n|\hat{\boldsymbol{\mu}}_{q''}|0\rangle}{(\Delta_n)^2}. \quad (12.41)$$

A problem with the SOS method is its slow convergence and the fact that, whenever the expansion functions do not cover the energy continuum, the result is incomplete.

Example 1. The hydrogen atom in an electric field – perturbational approach

An atom or molecule, when located in electric field undergoes a *deformation*. We will show this in detail, taking the example of the hydrogen atom.

First, let us introduce a Cartesian coordinate system, within which the whole event will be described. Let the electric field be directed towards your right, i.e. has the form $\boldsymbol{\mathcal{E}} = (\mathcal{E}, 0, 0)$, with a constant $\mathcal{E} > 0$. The positive value of \mathcal{E} means, according to the definition of electric field intensity, that a positive unit charge would move along $\boldsymbol{\mathcal{E}}$, i.e. from left to right. Thus, the anode is on your left and the cathode on your right.

We will consider a weak electric field, therefore the perturbation theory is applicable; this means just small corrections to the unperturbed situation. In our case the first-order correction to the wave function (see eq. (5.25)) will be expanded in the series of hydrogen atoms orbitals (they form the complete set,²³ cf. Chapter 5)

$$\psi_0^{(1)} = \sum_{k(\neq 0)} \frac{\langle k|\hat{H}^{(1)}|0\rangle}{-\frac{1}{2} - E_k^{(0)}} \psi_k^{(0)}, \quad (12.42)$$

²²Because μ^2 has the dimension of charge² × length², and Δ_n has the dimension of energy as for example in Coulombic energy: charge²/length.

²³Still they do not span the continuum.

where $|k\rangle \equiv \psi_k^{(0)}$ with energy $E_k^{(0)} = -\frac{1}{2n^2}$ (n is the principal quantum number of the state k) denotes the corresponding wave function of the hydrogen atom, $\hat{H}^{(1)}$ is the perturbation, which for a homogeneous electric field has the form $\hat{H}^{(1)} = -\hat{\boldsymbol{\mu}} \cdot \boldsymbol{\mathcal{E}} = -\hat{\mu}_x \mathcal{E}$, and $\hat{\mu}_x$ is the dipole moment operator (its x component). The operator, according to eq. (12.29), represents the sum of products: charge (in our case of the electron or proton) times the x coordinate of the corresponding particle (let us denote them x and X , respectively): $\hat{\mu}_x = -x + X$, where the atomic units have been assumed. To keep the expression as simple as possible, let us locate the proton at the origin of the coordinate system, i.e. $X = 0$. Finally, $\hat{H}^{(1)} = x\mathcal{E}$, because the electron charge is equal²⁴ to -1 . Thus the perturbation $\hat{H}^{(1)}$ is simply proportional to the x coordinate of the electron.²⁵

In order not to work in vain, let us first check which unperturbed states k will contribute to the summation on the right-hand side of (12.42). The ground state ($k = 0$), i.e. the $1s$ orbital is excluded (by the perturbation theory), next, $k = 1, 2, 3, 4$ denote the orbitals $2s, 2p_x, 2p_y, 2p_z$. The contribution of the $2s$ is equal to zero, because $\langle 2s|\hat{H}^{(1)}|1s\rangle = 0$ due to the antisymmetry of the integrand with respect to reflection $x \rightarrow -x$ ($\hat{H}^{(1)}$ changes its sign, while the orbitals $1s$ and $2s$ do not). A similar argument excludes the $2p_y$ and $2p_z$ orbitals. Hence, for the time being we have only a single candidate²⁶ $2p_x$. This time the integral is not zero and we will calculate it in a minute. If the candidates from the next shell ($n = 3$) are considered, similarly, the only non-zero contribution comes from $3p_x$. We will however stop our calculation at $n = 2$, because our goal is only to show how the whole machinery works. Thus, we need to calculate

$$\frac{\langle 2p_x|\hat{H}^{(1)}|1s\rangle}{E_0^{(0)} - E_1^{(0)}} = \frac{\langle 2p_x|x|1s\rangle}{E_0^{(0)} - E_1^{(0)}}\mathcal{E}.$$

The denominator is equal to $-1/2 + 1/8 = -3/8$ a.u. Calculation of the integral (a fast exercise for students²⁷) gives 0.7449 a.u. At $\mathcal{E} = 0.001$ a.u. we obtain the coefficient -0.001986 at the normalized orbital $2p_x$ in the first-order correction to the wave function. The negative value of the coefficient means that the orbital

²⁴It is, therefore, the operator of multiplication by x times a constant \mathcal{E} .

²⁵The proton might be located anywhere. The result does not depend on this choice, because the perturbation operators will differ by a constant. This, however, means that the nominator $\langle k|\hat{H}^{(1)}|1s\rangle$ in the formula will remain unchanged, because $\langle k|1s\rangle = 0$.

²⁶Note how fast our computation of the integrals proceeds. The main job (zero or not zero – that is the question) is done by the group theory.

²⁷From p. 181 we have

$$\begin{aligned} \langle 2p_x|x|1s\rangle &= \frac{1}{4\pi\sqrt{2}} \int_0^\infty dr r^4 \exp\left(-\frac{3}{2}r\right) \int_0^\pi d\theta \sin^3\theta \int_0^{2\pi} d\phi \cos^2\phi \\ &= \frac{1}{4\pi\sqrt{2}} 4! \left(\frac{3}{2}\right)^{-5} \frac{4}{3} \pi = 0.7449, \end{aligned}$$

where we have used the formula $\int_0^\infty x^n \exp(-\alpha x) dx = n! \alpha^{-(n+1)}$ to calculate the integral over r .

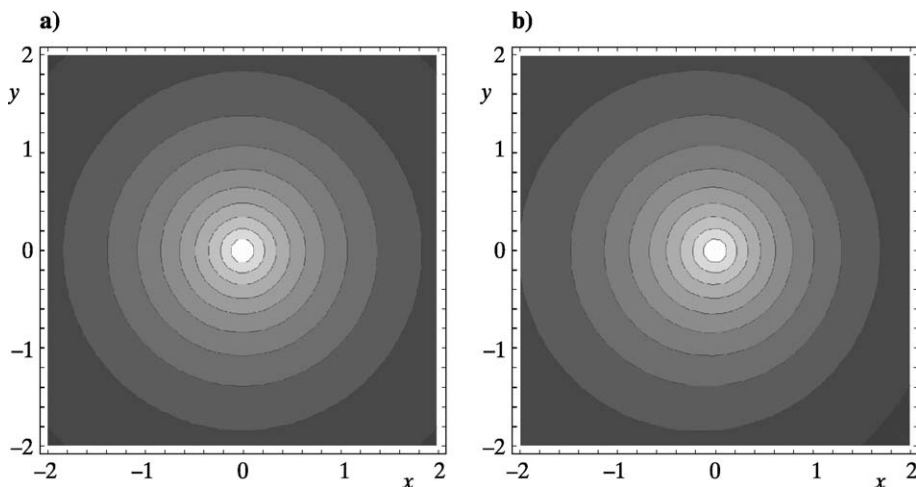


Fig. 12.5. Polarization of the hydrogen atom in an electric field. The wave function for (a) the unperturbed atom (b) the atom in the electric field (a.u.) $\mathcal{E} = (0.1, 0, 0)$. As we can see, there are differences in the corresponding electronic density distributions: in the second case the wave function is deformed towards the anode (i.e. leftwards). Please note that the wave function is less deformed in the region close to the nucleus, than in its left or right neighbourhood. This is a consequence of the fact that the deformation is made by the $-0.1986(2p_x)$ function. Its main role is to subtract on the right and add on the left, and the smallest changes are at the nucleus, because $2p_x$ has its node there.

$-0.001986(2p_x)$ has its positive lobe oriented leftward.²⁸ The small absolute value of the coefficient results in such a tiny modification of the $1s$ orbital after the electric field is applied, that it will be practically invisible in Fig. 12.5. In order to make the deformation visible, let us use $\mathcal{E} = 0.1$ a.u. Then, the admixture of $2p_x$ is equal to $-0.1986(2p_x)$, i.e. an approximate wave function of the hydrogen atom has the form: $1s - 0.19862p_x$. Fig. 12.5 shows the unperturbed and perturbed $1s$ orbital. As seen, the deformation makes an egg-like shape of the wave function (from a spherical one) – the electron is pulled towards the anode.²⁹ This is what we expected. Higher expansion functions ($3p_x, 4p_x, \dots$) would change the shape of the wave function by only a small amount.

Just *en passant* we may calculate an approximation to the dipole polarizability α_{xx} . From (12.40) we have

$$\alpha_{xx} \cong \frac{16}{3} \langle 2p_x | x(1s) \rangle^2 = \frac{16}{3} (0.7449)^2 = 2.96 \text{ a.u.}$$

The exact (non-relativistic) result is $\alpha_{xx} = 4.5$ a.u. This shows that the number we have received is somewhat off, but after recalling that only a single expansion

²⁸ $2p_x \equiv x \times$ the positive spherically symmetric factor, means the positive lobe of the $2p_x$ orbital is on your right (i.e. on the positive part of the x axis).

²⁹This “pulling” results from adding together $1s$ and (with a negative coefficient) $2p_x$, i.e. we decrease the probability amplitude on the right-hand side of the nucleus, and increase it on the left-hand side.

function has been used (instead of infinity of them) we should be quite happy with our result.³⁰

12.4.2 FINITE FIELD METHOD

The above calculation represents an example of the application to an atom of what is called the finite field method. In this method we solve the Schrödinger equation for the system in a given homogeneous (weak) electric field. Say, we are interested in the approximate values of $\alpha_{qq'}$ for a molecule. First, we choose a coordinate system, fix the positions of the nuclei in space (the Born–Oppenheimer approximation) and calculate the number of electrons in the molecule. These are the data needed for the input into the reliable method we choose to calculate $E(\mathcal{E})$. Then, using eqs. (12.38) and (12.24) we calculate the permanent dipole moment, the dipole polarizability, the dipole hyperpolarizabilities, etc. by approximating $E(\mathcal{E})$ by a power series of \mathcal{E}_q 's.

How do we put the molecule in an electric field? For example, at a long distance from the molecule we locate two point-like electric charges q_x and q_y on x and y axes, respectively. Hence, the total external field at the origin (where the “centre” of the molecule is located) has the components $\mathcal{E}_x = \frac{q_x}{R_x^2}$ and $\mathcal{E}_y = \frac{q_y}{R_y^2}$, with R_x and R_y denoting the distances of both charges from the origin. The field on the molecule will be almost homogeneous, because of the long R_x and R_y distances. In our case the $E(\mathcal{E})$ of eq. (12.24) reads as:

$$E(\mathcal{E}) = E^{(0)} - \mu_{0,x}\mathcal{E}_x + \mu_{0,y}\mathcal{E}_y - \frac{1}{2}\alpha_{xx}\mathcal{E}_x^2 - \frac{1}{2}\alpha_{xy}\mathcal{E}_x\mathcal{E}_y - \frac{1}{2}\alpha_{yx}\mathcal{E}_x\mathcal{E}_y - \frac{1}{2}\alpha_{yy}\mathcal{E}_y^2 + \dots \quad (12.43)$$

Neglecting the cubic and higher terms for a very small field \mathcal{E} (approximation) we obtain an equation for α_{xx} , α_{xy} and α_{yy} , because the polarizability tensor is symmetric. Note that

- $E(\mathcal{E}) - E^{(0)}$, as well as the components $\mu_{0,x}$, $\mu_{0,y}$ can be calculated;
- there is only one equation, while we have three unknowns to calculate. However, we may apply two other electric fields, which gives us two other equations.³¹

The results of the above procedure depend very much on the configuration of the point-charges. This is why the additional term $-\hat{\mu} \cdot \mathcal{E}$ in the Hamiltonian of the system is much more popular, which, according to eq. (12.11), is equivalent to immersing the system in a homogeneous electric field \mathcal{E} .

Example 2. Hydrogen atom in electric field – variational approach

The polarizability of the hydrogen atom may also be computed by using the variational method (Chapter 5), in which the variational wave function $\psi = \chi_1 + c\chi_2$

³⁰Such a situation is quite typical in the practice of quantum chemistry: the first terms of expansions give a lot, while next ones give less and less, the total result approaching, with more and more pain, its limit. Note that in the present case all terms are of the same sign, and we obtain better and better approximations when the expansion becomes longer and longer.

³¹We try to apply small fields, because then the hyperpolarizabilities play a negligible role (the cubic terms in the field intensity will be negligibly small).

where $\chi_1 \equiv 1s$ plus an admixture (as variational parameter) of the p type orbital χ_2 with a certain exponential coefficient ζ (Ritz method of Chapter 5), see Appendix V, eq. (V.1). From eq. (V.4), it can be seen that if χ_2 is taken as the $2p_x$ orbital (i.e. $\zeta = \frac{1}{2}$) we obtain $\alpha_{xx} = 2.96$ a.u., the same number we have already obtained by the perturbational method. If we take $\zeta = 1$ i.e. the same as in hydrogenic orbital $1s$, we will obtain $\alpha_{xx} = 4$ a.u. Well, a substantial improvement.

Is it possible to obtain an even better result with the variational function ψ ? Yes, it is. If we use the finite field method (with the electric field equal $\mathcal{E} = 0.01$ a.u.), we will obtain³² the minimum of E of eq. (V.3) as corresponding to $\zeta_{\text{opt}} = 0.797224$. If we insert $\zeta = \zeta_{\text{opt}}$ into eq. (V.4), we will obtain 4.475 a.u., only 0.5% off the exact result. This nearly perfect result is computed with a single correction function!³³

Sadlej relation

In order to compute accurate values of $E(\mathcal{E})$ extended LCAO expansions have to be used. Andrzej Sadlej³⁴ noticed that this huge numerical task in fact only takes into account a very simple effect: just a kind of *shift*³⁵ of the electronic charge distribution towards the anode. Since the atomic orbitals are usually centred on the nuclei and the electronic charge distribution shifts, compensation (still using the on-nuclei atomic orbitals) requires monstrous and expensive LCAO expansions.

In LCAO calculations, nowadays, we most often use Gaussian-type orbitals (GTO, see Chapter 8). They are rarely thought of as representing wave functions of the harmonic oscillator³⁶ (cf. Chapter 4), but they really do. Sadlej became interested in what would happen if an electron described by a GTO were subject to the electric field \mathcal{E} .

Sadlej noticed that the Gaussian type orbital will change in a similar way to the wave functions of a charged harmonic oscillator in electric field. These however simply shift.

Indeed, this can be shown as follows. The Schrödinger equation for the harmonic oscillator (here: an electron with $m = 1$ in a.u., its position is x) without any electric field is given on p. 166. The Schrödinger equation for an electron oscillating in homogeneous electric field $\mathcal{E} > 0$ has the form:

$$\left(-\frac{1}{2} \frac{d^2}{dx^2} + \frac{1}{2} kx^2 + \mathcal{E}x\right) \psi(x, \mathcal{E}) = E(\mathcal{E}) \psi(x, \mathcal{E}). \quad (12.44)$$

³²You may use *Mathematica* and the command FindMinimum[$E, \{\zeta, 1\}$].

³³This means that sometimes long expansions in the Ritz method may result from an unfortunate choice of expansion functions.

³⁴A.J. Sadlej, *Chem. Phys. Letters* 47 (1977) 50; A.J. Sadlej, *Acta Phys. Polon. A* 53 (1978) 297.

³⁵With a deformation.

³⁶At least if they represent the $1s$ GTOs.

Now, let us find such constants a and b , that:

$$\frac{1}{2}kx^2 + \mathcal{E}x = \frac{1}{2}k(x - a)^2 + b. \quad (12.45)$$

We immediately get $a = -\mathcal{E}/k$, $b = -\frac{1}{2}ka^2$. The constant b is completely irrelevant, since it only shifts the zero on the energy scale. Thus,

the solution to a charged harmonic oscillator (oscillating electron) in a homogeneous electric field represents the same function as for the harmonic oscillator without the field, but shifted by $-\frac{\mathcal{E}}{k}$.

Indeed, inserting $x' = x + \frac{\mathcal{E}}{k}$ leads to $d/dx = d/dx'$ and $d^2/dx^2 = d^2/dx'^2$ which gives a similar Schrödinger equation except that the harmonic potential is shifted. Therefore, the solution to the equation can be written as simply a shifted zero-field solution $\psi(x') = \psi(x + \frac{\mathcal{E}}{k})$. This is quite understandable, because the operation means nothing more than adding to the parabolic potential energy $kx^2/2$ a term proportional to x , i.e. again a parabola potential (a displaced one though, Fig. 12.6.b).

To see how this displacement depends on the GTO *exponent*, let us recall its relation to the harmonic oscillator force constant k (cf. Chapter 4). The harmonic oscillator eigenfunction corresponds to a Gaussian orbital with an exponent equal to $\alpha/2$, where $\alpha^2 = k$ (in a.u.). Therefore, if we have a GTO with exponent equal to A ,

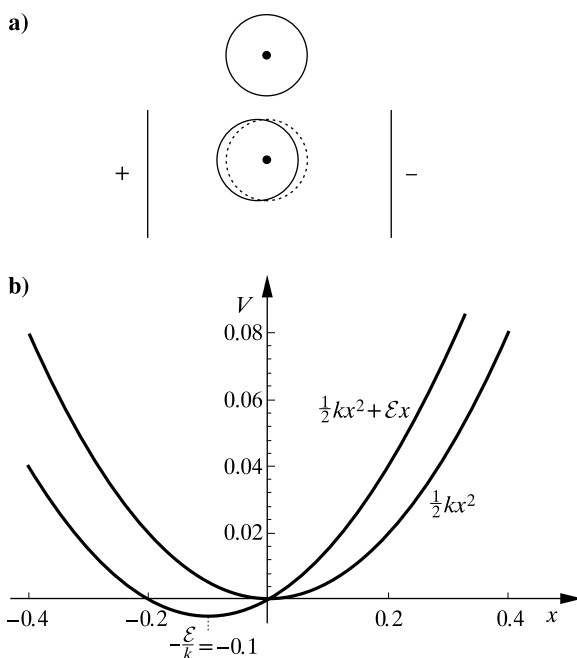


Fig. 12.6. Sadlej relation. The electric field mainly causes a shift of the electronic charge distribution towards the anode (a). A Gaussian type orbital represents the eigenfunction of a harmonic oscillator. Suppose an electron oscillates in a parabolic potential energy well (with the force constant k). In this situation a homogeneous electric field \mathcal{E} corresponds to the perturbation $\mathcal{E}x$, that *conserves the harmonicity with unchanged force constant k* (Fig. b).

this means the corresponding harmonic oscillator has the force constant $k = 4A^2$. Now, if the homogeneous electric field \mathcal{E} is switched on, the centre of this atomic orbital has to move by $\Delta(A) = -\mathcal{E}/k = -\frac{1}{4}\mathcal{E}/A^2$. This means that all the atomic orbitals have to move opposite to the applied electric field (as expected) and the displacement of the orbital is small, if its exponent is large, and *vice versa*. Also, if the atomic electron charge distribution results from several GTOs (as in the LCAO expansion) it deforms in the electric field in such a way that the diffuse orbitals shift a certain amount, while the compact ones (with large exponents) shift by only a small amount. Altogether this does not mean just a simple shift of the electronic charge density, it means that instead its shift is accompanied by a deformation. On the other hand, we may simply optimize the GTO positions within the finite field Hartree–Fock method, and check whether the corresponding shifts $\Delta_{\text{opt}}(A)$ indeed follow the Sadlej relation.³⁷ It turns out that the relation $\Delta_{\text{opt}}(A) \sim -\mathcal{E}/A^2$ is satisfied to a good accuracy,³⁸ despite the fact that the potential energy in an atom does not represent a parabola.

The electrostatic catastrophe of the theory

There is a serious problem in finite field theory. If even the *weakest* homogeneous electric field is applied and a very good basis set is used, we are *bound* to have some kind of catastrophe. A nasty word, but unfortunately reflecting quite adequately a mathematical horror we are going to be exposed to after adding to the Hamiltonian operator $\hat{H}^{(1)} = x\mathcal{E}$, here x symbolizes the component of the dipole moment.³⁹ The problem is that this operator is *unbound*, i.e. for a normalized trial function ϕ the integral $\langle \phi | \hat{H}^{(1)} | \phi \rangle$ may attain ∞ or $-\infty$. Indeed, by gradually shifting the function ϕ towards the negative values of the x axis, we obtain more and more negative values of the integral, and for $x = -\infty$ we get $\langle \phi | \hat{H}^{(1)} | \phi \rangle = -\infty$. In other words,

when using atomic orbitals centred far from the nuclei in the region of the negative x (or allowing optimization of the orbital centres with the field switched on), we will lower the energy to $-\infty$, i.e. we obtain a catastrophe. This is quite understandable, because such a system (electrons separated from the nuclei and shifted far away along the x axis) has a huge dipole moment, and therefore *very low energy*.

³⁷We have tacitly assumed that in the unperturbed molecule the atomic orbitals occupy optimal positions. This assumption may sometimes cause trouble. If the centres of the atomic orbitals in an isolated molecule are non-optimized, we may end up with a kind of antipolarizability: we apply the electric field and, when the atomic orbital centres are optimized, the electron cloud moves opposite to that which we expect. This is possible only because in such a case the orbital centres mainly follow the strong intramolecular electric field, rather than the much weaker external field \mathcal{E} (J.M. André, J. Delhalle, J.G. Fripiat, G. Hennico, L. Piela, *Intern. J. Quantum Chem.* 22S (1988) 665).

³⁸This is how the *electric-field-variant orbitals* (EFVO) were born: Andrzej's colleagues did not believe in this simple recipe for calculating polarizabilities, but they lost the bet (a bar of chocolate).

³⁹The most dramatic form of the problem would appear if the finite field method was combined with the numerical solution of the Schrödinger or Fock equation.

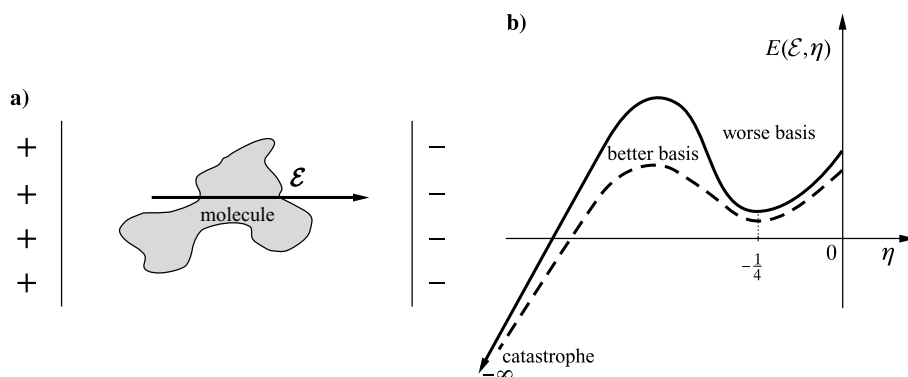


Fig. 12.7. A molecule in a homogeneous electric field (a). In Fig. (b) η is a parameter describing the shift $\eta\mathcal{E}/A^2$ of the Gaussian atomic orbitals along the electric field \mathcal{E} , with $\eta = 0$ showing the centring on the nuclei. The total energy $E(\mathcal{E}, \eta)$ is a function of the electric field intensity \mathcal{E} and the basis set shift parameter η . Optimization of η gives a result close to the Sadlej value $\eta = -\frac{1}{4}$, larger $|\eta|$ values first lead to an increase of E , but then to a decrease towards a catastrophe: $\lim_{\eta \rightarrow -\infty} E(\mathcal{E}, \eta) = -\infty$.

Suppose the calculations for a molecule in an electric field \mathcal{E} are carried out. According to the Sadlej relation, we shift the corresponding atomic orbitals proportionally to $\eta\mathcal{E}/A^2$, with $\eta \leq 0$, and the energy goes down. Around $\eta = -\frac{1}{4}$, which according to Sadlej corresponds to optimal shifts,⁴⁰ we may expect the lowest energy, then, for larger $|\eta|$, the energy has to go up. What if we continue to increase (Fig. 12.7) the shift parameter $|\eta|$?

The energy increase will continue only up to some critical value of η . Then, according to the discussion above, the energy will fall to $-\infty$, i.e. to a catastrophe. Thus the energy curve exhibits a barrier (Fig. 12.7), that is related to the basis set quality (its “saturation”). A poor basis means a high barrier and the ideal basis (i.e. the complete basis set), gives no barrier at all, just falling into the abyss with the polarizability going to infinity, etc. Therefore, rather paradoxically, reliable values of polarizability are obtained using a medium quality basis set. An improvement of the basis will lead to worse results.⁴¹

The above relate to variational calculations. What about the perturbational method? In the first- and second-order corrections to the energy, the formulae contain the zero-order approximation to the wave function $\psi_0^{(0)}$, e.g., $E^{(2)} = \langle \psi_0^{(0)} | \hat{H}^{(1)} \psi_0^{(1)} \rangle$. If the origin of the coordinate system is located on the molecule, then the exponential decay of $\psi_0^{(0)}$ forces the first-order correction to the wave function $\psi_0^{(1)}$ to be also localized close to the origin, otherwise it would tend to zero through the shifting towards the negative values of x (this prevents the integral diverging to $-\infty$). However, the third-order correction to the energy contains the term $\langle \psi_0^{(1)} | \hat{H}^{(1)} \psi_0^{(1)} \rangle$, which may already go to $-\infty$. Hence, the perturbation theory also carries the seed of future electrostatic catastrophe.

⁴⁰They are optimal for a parabolic potential.

⁴¹Once more in this book: excessive wealth does not improve life.

12.4.3 WHAT IS GOING ON AT HIGHER ELECTRIC FIELDS

Polarization

The theory described so far is applicable only when the electric field intensity is small. Such a field can polarize (a small deformation) the electronic charge distribution. More fascinating phenomena begin when the electric field gets stronger.

Deformation

Of course, the equilibrium configurations of the molecule with and without an electric field differ. In a simple case, say the HCl molecule, the HCl distance increases in an electric field. It has to increase, since the cathode pulls the hydrogen atom and repels the chlorine atom, while the anode does the opposite. In more complex cases, like a flexible molecule, the field may change its conformation. This means that the polarizability results both from the electron cloud deformation and the displacement of the nuclei. It turns out that the later effect (called vibrational polarization) is of great importance.⁴²

Dissociation

When the electric field gets stronger the molecule may dissociate into ions. To this end, the external electric field intensity has to become comparable to the electric field produced by the molecule itself in its neighbourhood. The intramolecular electric fields are huge, the intermolecular ones are weaker but also very large, of the order of 10^8 V/m, much larger than those offered by current technical installations. No wonder then, that the molecules may interact to such an extent that they may even undergo chemical reactions. When the interaction is weaker, the electric fields produced by molecules may lead to intermolecular complexes, many beautiful examples may be found in biochemistry (see Chapters 13 and 15). A strong external electric field applied to a crystal may cause a cascade of processes, e.g., the so called *displacive phase transitions*, when sudden displacements of atoms occur, and a new crystal structure appears.

displacive
phase transition

Destruction

A sufficiently strong electric field will destroy the molecules through their ionization. The resulting ions accelerate in the field, collide with the molecules and ionize them even more (these phenomena are accompanied by light emission as in vacuum tubes). Such processes may lead to the final decomposition of the system (plasma) with the electrons and the nuclei finally reaching the anode and cathode. We will have a vacuum.

Creation!

Let us keep increasing the electric field applied to the vacuum. Will anything interesting happen? We know, from Chapter 3, that when huge electric field intensities

⁴²J.-M. André, B. Champagne, in *“Conjugated Oligomers, Polymers, and Dendrimers: From Polyacetylene to DNA”*, J.L. Brédas (ed.), Bibliothèque Scientifique Francqui, De Boeck Université, p. 349.

are applied (of the order of the electric field intensity in the vicinity of a proton – not feasible for the time being), then *the particles and antiparticles will leap out of the vacuum!* The vacuum is not just nothing. Formula (3.71) gives the probability of such a process.

12.5 A MOLECULE IN AN OSCILLATING ELECTRIC FIELD

Constant and oscillating components

A non-zero hyperpolarizability indicates a *non-linear* response (contributions to the dipole moment proportional to the second and higher powers of the field intensity). This may mean an “inflated” reaction to the applied field, a highly desired feature for contemporary optoelectronic materials. One such reaction is the second- and third-harmonic generation (SHG and THG, respectively), where light of frequency ω generates in a material light with frequencies 2ω and 3ω , respectively. A simple statement about why this may happen is shown below.⁴³

Let us imagine a molecule immobilized in a laboratory coordinate system (like in an oriented crystal). Let us switch on a homogeneous electric field \mathcal{E} , which has two components, a static component \mathcal{E}^0 and an oscillating one \mathcal{E}^ω with frequency ω :

$$\mathcal{E} = \mathcal{E}^0 + \mathcal{E}^\omega \cos(\omega t). \quad (12.46)$$

We may imagine various experiments here: the steady field along x , y or z and a light beam polarized along x , y or z , we may also vary ω for each beam, etc. Such choices lead to a rich set of non-linear optical phenomena.⁴⁴ What will the reaction of the molecule be in such an experiment? Let us see.⁴⁵

Induced dipole moment

The total dipole moment of the molecule (i.e. the permanent moment μ_0 plus the induced moment μ_{ind}) will depend on time, because μ_{ind} does:

$$\mu_q(t) = \mu_{0,q} + \mu_{\text{ind},q}, \quad (12.47)$$

$$\begin{aligned} \mu_{\text{ind},q}(t) = & \sum_{q'} \alpha_{qq'} \mathcal{E}_{q'} + \frac{1}{2} \sum_{q'q''} \beta_{qq'q''} \mathcal{E}_{q'} \mathcal{E}_{q''} \\ & + \frac{1}{6} \sum_{q',q'',q'''} \gamma_{qq'q''q'''} \mathcal{E}_{q'} \mathcal{E}_{q''} \mathcal{E}_{q'''} + \dots \end{aligned} \quad (12.48)$$

Therefore, if we insert $\mathcal{E}_q = \mathcal{E}_q^0 + \mathcal{E}_q^\omega \cos(\omega t)$ as the electric field component for

⁴³The problem of how the polarizability changes as a function of inducing wave frequency is described in detail in J. Olsen, P. Jørgensen, *J. Chem. Phys.* 82 (1985) 3235.

⁴⁴S. Kielich, “*Molecular non-linear optics*”, Warszawa–Poznań, PWN (1977).

⁴⁵For the sake of simplicity we have used the same frequency and the same phases for the light polarized along x , y and z .

$q = x, y, z$, we obtain

$$\begin{aligned}
 \mu_q(t) = & \mu_{0,q} + \sum_{q'} \alpha_{qq'} [\mathcal{E}_{q'}^0 + \mathcal{E}_{q'}^\omega \cos(\omega t)] \\
 & + \frac{1}{2} \sum_{q',q''} \beta_{qq'q''} [\mathcal{E}_{q'}^0 + \mathcal{E}_{q'}^\omega \cos(\omega t)] \times [\mathcal{E}_{q''}^0 + \mathcal{E}_{q''}^\omega \cos(\omega t)] \\
 & + \frac{1}{6} \sum_{q',q'',q'''} \gamma_{qq'q''q'''} [\mathcal{E}_{q'}^0 + \mathcal{E}_{q'}^\omega \cos(\omega t)] [\mathcal{E}_{q''}^0 + \mathcal{E}_{q''}^\omega \cos(\omega t)] \\
 & \times [\mathcal{E}_{q'''}^0 + \mathcal{E}_{q'''}^\omega \cos(\omega t)] + \dots
 \end{aligned} \tag{12.49}$$

Second (SHG) and Third (THG) Harmonic Generation

After multiplication and simple trigonometry we have

$$\mu_q(t) = \mu_{\omega=0,q} + \mu_{\omega,q} \cos \omega t + \mu_{2\omega,q} \cos(2\omega t) + \mu_{3\omega,q} \cos(3\omega t), \tag{12.50}$$

where the amplitudes μ corresponding to the coordinate $q \in x, y, z$ and to the particular resulting frequencies $0, \omega, 2\omega, 3\omega$ have the following form⁴⁶

$$\begin{aligned}
 \mu_{\omega=0,q} = & \mu_{0,q} + \sum_{q'} \alpha_{qq'}(0; 0) \mathcal{E}_{q'}^0 + \frac{1}{2} \sum_{q',q''} \beta_{qq'q''}(0; 0, 0) \mathcal{E}_{q'}^0 \mathcal{E}_{q''}^0 \\
 & + \frac{1}{6} \sum_{q',q'',q'''} \gamma_{qq'q''q'''}(0; 0, 0, 0) \mathcal{E}_{q'}^0 \mathcal{E}_{q''}^0 \mathcal{E}_{q'''}^0 \\
 & + \frac{1}{4} \sum_{q',q''} \beta_{q,q',q''}(0; -\omega, \omega) \mathcal{E}_{q'}^\omega \mathcal{E}_{q''}^\omega \\
 & + \frac{1}{4} \sum_{q',q'',q'''} \gamma_{qq'q''q'''}(0; 0, -\omega, \omega) \mathcal{E}_{q'}^0 \mathcal{E}_{q''}^\omega \mathcal{E}_{q'''}^\omega, \\
 \mu_{\omega,q} = & \sum_{q'} \alpha_{qq'}(-\omega; \omega) \mathcal{E}_{q'}^\omega + \sum_{q',q''} \beta_{qq'q''}(-\omega; \omega, 0) \mathcal{E}_{q'}^\omega \mathcal{E}_{q''}^0 \\
 & + \frac{1}{2} \sum_{q',q'',q'''} \gamma_{qq'q''q'''}(-\omega; \omega, 0, 0) \mathcal{E}_{q'}^\omega \mathcal{E}_{q''}^0 \mathcal{E}_{q'''}^0
 \end{aligned}$$

⁴⁶According to convention, a given (hyper)polarizability, e.g., $\gamma_{qq'q''q'''}(-3\omega; \omega, \omega, \omega)$, is accompanied (in parenthesis) by the frequencies ω corresponding to the three directions x, y, z of the incident light polarization (here: q', q'' and q''' , preceded by minus the Fourier frequency of the term, -3ω , which symbolizes the photon energy conservation law). Some of the symbols, e.g., $\gamma_{qq'q''q'''}(-\omega; \omega, -\omega, \omega)$, after a semicolon have negative values, which means a partial (as in $\gamma_{qq'q''q'''}(-\omega; \omega, -\omega, \omega)$) or complete (as in $\beta_{q,q',q''}(0; -\omega, \omega)$) cancellation of the intensity of the oscillating electric field.

$$\begin{aligned}
& + \frac{1}{8} \sum_{q', q'', q'''} \gamma_{qq'q''q'''}(-\omega; \omega, -\omega, \omega) \mathcal{E}_{q'}^{\omega} \mathcal{E}_{q''}^{\omega} \mathcal{E}_{q'''}^{\omega}, \\
\mu_{2\omega, q} = & \frac{1}{4} \sum_{q' q''} \beta_{q, q', q''}(-2\omega; \omega, \omega) \mathcal{E}_{q'}^{\omega} \mathcal{E}_{q''}^{\omega} \\
& + \frac{1}{4} \sum_{q', q'', q'''} \gamma_{qq'q''q'''}(-2\omega; \omega, \omega, 0) \mathcal{E}_{q'}^{\omega} \mathcal{E}_{q''}^{\omega} \mathcal{E}_{q'''}^0, \quad (12.51)
\end{aligned}$$

$$\mu_{3\omega, q} = \frac{1}{24} \sum_{q', q'', q'''} \gamma_{qq'q''q'''}(-3\omega; \omega, \omega, \omega) \mathcal{E}_{q'}^{\omega} \mathcal{E}_{q''}^{\omega} \mathcal{E}_{q'''}^{\omega}. \quad (12.52)$$

We see that:

- An oscillating electric field may result in a non-oscillating dipole moment related to the hyperpolarizabilities $\beta_{q, q', q''}(0; -\omega, \omega)$ and $\gamma_{qq'q''q'''}(0; 0, -\omega, \omega)$, which manifests as an electric potential difference on two opposite crystal faces.
- The dipole moment oscillates with the basic frequency ω of the incident light and in addition, with two other frequencies: the second (2ω) and third (3ω) harmonics (SHG and THG, respectively). This is supported by experiment (mentioned in the example at the beginning of the chapter), applying incident light of frequency ω we obtain emitted light with frequencies⁴⁷ 2ω and 3ω .

Note that to generate a large second harmonic the material has to have large values of the hyperpolarizabilities β and γ . The THG needs a large γ . In both cases a strong laser electric field is necessary. The SHG and THG therefore require support from the theoretical side: we are looking for high hyperpolarizability materials and quantum mechanical calculations may predict such materials *before* an expensive organic synthesis is done.⁴⁸

MAGNETIC PHENOMENA

The electric and magnetic fields (both of them are related by the Maxwell equations, Appendix G) interact differently with matter, which is highlighted in Fig. 12.8, where the electron trajectories in both fields are shown. They are totally different, the trajectory in the magnetic field has a cycloid character, while in the electric field it is a parabola. This is why the description of magnetic properties differs so much from that of electric properties.

⁴⁷This experiment was first carried out by P.A. Franken, A.E. Hill, C.W. Peters, G. Weinreich, *Phys. Rev. Letters* 7 (1961) 118.

⁴⁸In molecular crystals it is not sufficient that particular molecules have high values of hyperpolarizability. What counts is the hyperpolarizability of the crystal unit cell.

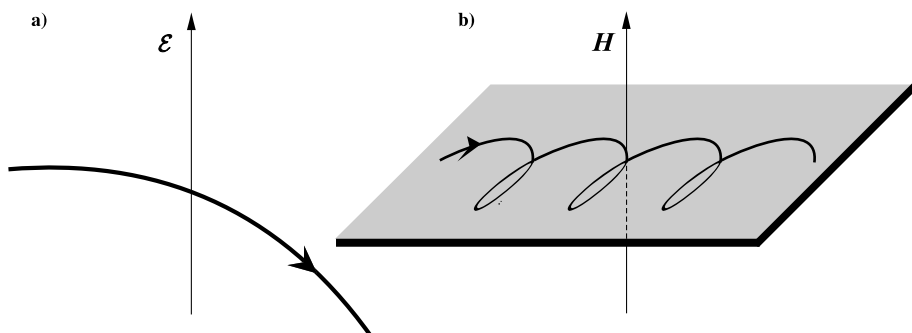


Fig. 12.8. The trajectories of an electron in the (a) electric field – the trajectory is a parabola (b) magnetic field, perpendicular to the incident velocity – the trajectory is a cycloid in a plane perpendicular to the figure.

12.6 MAGNETIC DIPOLE MOMENTS OF ELEMENTARY PARTICLES

12.6.1 ELECTRON

An elementary particle, besides its orbital angular momentum, may also have internal angular momentum, or spin, cf. p. 25. In Chapter 3, the Dirac theory led to a relation between the *spin* angular momentum s of the electron and its *dipole magnetic moment* $M_{\text{spin,el}}$ (eq. (3.62), p. 122):

$$M_{\text{spin,el}} = \gamma_{\text{el}} s,$$

with the *gyromagnetic factor*⁴⁹

$$\gamma_{\text{el}} = -2 \frac{\mu_B}{\hbar},$$

where the Bohr magneton (m_0 is the electronic rest mass)

$$\mu_B = \frac{e\hbar}{2m_0c}.$$

The relation is quite a surprise, because the gyromagnetic factor is twice as large as that appearing in the relation between the electron *orbital* angular momentum L and the associated magnetic dipole moment

$$M_{\text{orb,el}} = -\frac{\mu_B}{\hbar} L. \quad (12.53)$$

Quantum electrodynamics explains this effect qualitatively – predicting a factor very close to the experimental value⁵⁰ 2.0023193043737, known with the breathtaking accuracy of ± 0.00000000000082 .

⁴⁹From the Greek word *gyros*, or circle; it is believed that a circular motion of a charged particle is related to the resulting magnetic moment.

⁵⁰R.S. Van Dyck Jr., P.B. Schwinberg, H.G. Dehmelt, *Phys. Rev. Letters* 59 (1990) 26.

magnetic dipole
moment

gyro-magnetic
factor

12.6.2 NUCLEUS

Let us stay within the Dirac theory. If, instead of an electron, we take a *nucleus* of charge $+Ze$ and atomic mass⁵¹ M , then we *would presume* (after insertion into the above formulae) the gyromagnetic factor should be $\gamma = 2 \frac{Z}{M} \frac{\mu_N}{\hbar}$, where $\mu_N = \frac{e\hbar}{2m_H c}$ (m_H denoting the proton mass) is known as the *nuclear magneton*.⁵² For a proton ($Z = 1$, $M = 1$), we would have $\gamma_p = 2\mu_N/\hbar$, whereas the experimental value⁵³ is $\gamma_p = 5.59\mu_N/\hbar$. What is going on? In both cases we have a single elementary particle (electron or proton), both have the spin quantum number equal to $\frac{1}{2}$, we might expect that nothing special will happen to the proton, and only the mass ratio and charge will make a difference. Instead we see that Dirac theory does relate to the electron, but not to the nuclei. Visibly, the proton is more complex than the electron. We see that even the simplest nucleus has internal machinery, which results in the observed strange deviation. There are lots of quarks in the proton (three valence quarks and a sea of virtual quarks together with the gluons, etc.). The proton and electron polarize the vacuum differently and this results in different gyromagnetic factors. Other nuclei exhibit even stranger properties. Sometimes we even have negative gyromagnetic coefficients. In such a case their magnetic moment is opposite to the spin angular momentum. The complex nature of the internal machinery of the nuclei and vacuum polarization lead to the observed gyromagnetic coefficients.⁵⁴ Science has had some success here, e.g., for leptons,⁵⁵ but for nuclei the situation is worse. This is why we are simply forced to take this into account in the present book⁵⁶ and treat the *spin magnetic moments* of the nuclei as the experimental data:

nuclear
magneton

$$\mathbf{M}_A = \gamma_A \mathbf{I}_A, \quad (12.54)$$

where \mathbf{I}_A represents the spin angular momentum of the nucleus A .

⁵¹Unitless quantity.

⁵²Ca. 1840 times smaller than the Bohr magneton (for the electron).

⁵³Also the gyromagnetic factor for an electron is expected to be ca. 1840 times larger than that for a proton. This means that a proton is expected to create a magnetic field ca. 1840 times weaker than the field created by an electron.

⁵⁴The relation between spin and magnetic moment is as mysterious as that between the magnetic moment and charge of a particle (the spin is associated with a rotation, while the magnetic moment is associated with a rotation of a charged object) or its mass. A neutron has spin equal to $\frac{1}{2}$ and magnetic moment similar to that of a proton despite the zero electric charge. The neutrino has no charge, nearly zero mass and magnetic moment, and still has a spin equal to $\frac{1}{2}$.

⁵⁵And what about the “heavier brothers” of the electron, the muon and taon (cf. p. 268)? For the muon, the coefficient in the gyromagnetic factor (2.0023318920) is similar to that of the electron (2.0023193043737), just a bit larger and agrees equally well with experiment. For the taon we have only a theoretical result, a little larger than for the two other “brothers”. Thus, each of the lepton family behaves in a similar way.

⁵⁶With a suitable respect of the Nature’s complexity.

12.6.3 DIPOLE MOMENT IN THE FIELD

Electric field

The problem of an electric dipole μ rotating in an electric field was described on p. 631. There we were interested in the ground state. When the field is switched off (cf. p. 176), the ground state is non-degenerate ($J = M = 0$). After a weak electric field (\mathcal{E}) is switched on, the ground-state wave function deforms in such a way as to prefer the alignment of the rotating dipole moment along the field. Since we may always use a complete set of rigid rotator wave functions (at zero field), this means the deformed wave functions *have to be linear combinations of the wave functions corresponding to different J* .

Magnetic field

Imagine a spinning top which is a magnet. If you make it spin (with angular momentum I) and leave it in space without any external torque τ , then due to the fact that space is isotropic, its angular momentum will stay constant, because $\frac{dI}{dt} = \tau = 0$ (τ is time), i.e. the top will rotate about its axis with a constant speed and the axis will not move with respect to distant stars, Fig. 12.9.a.

The situation changes if a magnetic field is switched on. Now, the space is no longer isotropic and the vector of the angular momentum is no longer conserved. However, the conservation law *for the projection of the angular momentum on the direction of the field* is still valid. This means that the top makes a precession about the

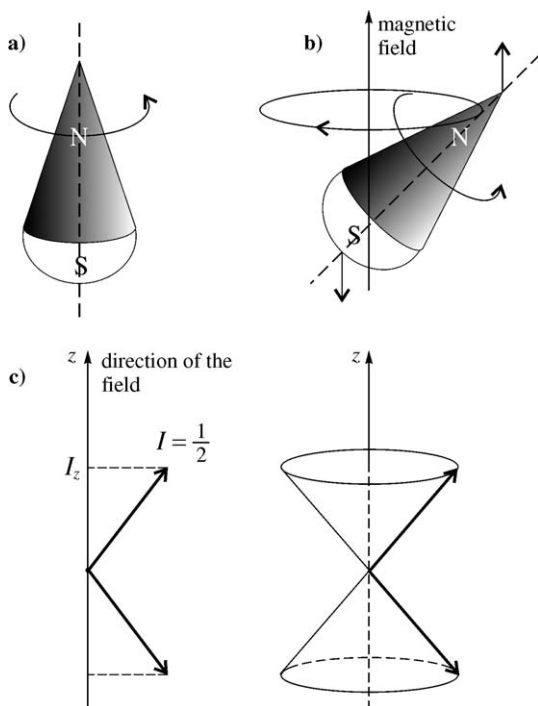


Fig. 12.9. Classical and quantum tops (magnets) in space. (a) The space is isotropic and therefore the classical top preserves its angular momentum I , i.e. its axis does not move with respect to distant stars and the top rotates about its axis with a constant speed. (b) The same top in a magnetic field. The space is no longer isotropic, and therefore the total angular momentum is no longer preserved. The projection of the total momentum on the field direction is still preserved. The magnetic field causes a torque τ (orthogonal to the picture) and $\frac{dI}{dt} = \tau$. This means precession of the top axis about the direction of the field. (c) A quantum top, i.e. an elementary particle with spin quantum number $I = \frac{1}{2}$ in the magnetic field. The projection I_z of its spin angular momentum I is quantized: $I_z = m_I \hbar$ with $m_I = -\frac{1}{2}, +\frac{1}{2}$ and, therefore, we have two energy eigenstates that correspond to two precession cones, directed up and down.

field axis, because $\frac{d\mathbf{I}}{dt} = \boldsymbol{\tau} \neq \mathbf{0}$, and $\boldsymbol{\tau}$ is orthogonal to \mathbf{I} and to the field, Fig. 12.9.b. In quantum mechanics the magnetic dipole moment $\mathbf{M} = \gamma\mathbf{I}$ in the magnetic field $\mathbf{H} = (0, 0, H)$, $H > 0$, has as many stationary states as is the number of possible projections of the spin angular momentum on the field direction. From Chapter 1, we know that this number is $2I + 1$, where I is the spin quantum number of the particle (e.g., for a proton: $I = \frac{1}{2}$). The projections are equal (Fig. 12.9.c) $m_I\hbar$ with $m_I = -I, -I + 1, \dots, 0, \dots, +I$. Therefore,

the energy levels in the magnetic field

$$E_{m_I} = -\gamma m_I \hbar H. \quad (12.55)$$

Note, that the energy level splitting is proportional to the magnetic field intensity, Fig. 12.10.

If a nucleus has $I = \frac{1}{2}$, then the energy difference ΔE between the two states in a magnetic field H : one with $m_I = -\frac{1}{2}$ and the other one with $m_I = \frac{1}{2}$, equals $\Delta E = 2 \times \frac{1}{2} \gamma \hbar H = \gamma \hbar H$, and

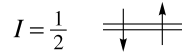
$$\Delta E = h\nu_L, \quad (12.56)$$

where the Larmor⁵⁷ frequency is defined as

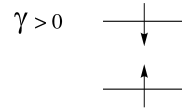
$$\nu_L = \frac{\gamma H}{2\pi}. \quad (12.57)$$

We see (Fig. 12.10) that for nuclei with $\gamma > 0$, lower energy corresponds to $m_I = \frac{1}{2}$, i.e. to the spin moment along the field (forming an angle $\theta = 54^\circ 44'$ with the magnetic field vector, see p. 28).

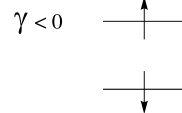
a) zero field



b) non-zero field



c) non-zero field



direction
of the field

direction
of the field

Fig. 12.10. Energy levels in magnetic field $\mathbf{H} = (0, 0, H)$ for a nucleus with spin angular momentum \mathbf{I} corresponding to spin quantum number $I = \frac{1}{2}$. The magnetic dipole moment equals to $\mathbf{M} = \gamma\mathbf{I}$ (a) at the zero field the level is doubly degenerate. (b) For $\gamma > 0$ (e.g., a proton) \mathbf{I} and \mathbf{M} have the same direction. In a non-zero magnetic field the energy equals to $E = -\mathbf{M} \cdot \mathbf{H} = -M_z H = -\gamma m_I \hbar H$, where $m_I = \pm \frac{1}{2}$. Thus, the degeneracy is lifted: the state with $m_I = \frac{1}{2}$, i.e. with the positive projection of \mathbf{I} on direction of the magnetic field has lower energy. (c) For $\gamma < 0$ \mathbf{I} and \mathbf{M} have the opposite direction. The state with $m_I = \frac{1}{2}$, i.e. has higher energy.

⁵⁷Joseph Larmor (1857–1942), Irish physicist, professor at Cambridge University.

Note that

there is a difference between the energy levels of the electric dipole moment in an electric field and the levels of the magnetic dipole in a magnetic field. The difference is that, for the magnetic dipole of an elementary particle the states do not have admixtures from the other I values (which is given by nature), while for the electric dipole there are admixtures from states with other values of J .

This suggests that we may also expect such admixtures in a magnetic field. In fact this is true if the particle is complex. For example, the singlet state ($S = 0$) of the hydrogen molecule gets an admixture of the triplet state ($S = 1$) in the magnetic field, because the spin magnetic moments of both electrons tend to align parallel to the field.

12.7 TRANSITIONS BETWEEN THE NUCLEAR SPIN QUANTUM STATES – NMR TECHNIQUE

Is there any possibility of making the nuclear spin flip from one quantum state to another? Yes. Evidently, we have to create distinct energy levels corresponding to different spin projections, i.e. to switch the magnetic field on, Figs. 12.10 and 12.11.a. After the electromagnetic field is applied and its frequency matches the energy level difference, the system absorbs the energy. It looks as if a nucleus absorbs the energy and changes its quantum state. In a genuine NMR experiment, the electromagnetic frequency is fixed (radio wave lengths) and the specimen is scanned by a variable magnetic field. At some particular field values the energy difference matches the electromagnetic frequency and the transition (Nuclear Magnetic Resonance) is observed.

The magnetic field that a particular nucleus feels differs from the external magnetic field applied, because the electronic structure in which the nucleus is immersed in, makes its own contribution (see Fig. 12.11.b,c). Also the nuclear spins interact by creating their own magnetic fields.

We have not yet considered these effects in the non-relativistic Hamiltonian (2.1) (e.g., no spin–spin or spin–field interactions). The effects which we are now dealing with are so small, of the order of 10^{-11} kcal/mole, that they are of no importance for most applications, including UV-VIS, IR, Raman spectra, electronic structure, chemical reactions, intermolecular interactions, etc. This time, however, the situation changes: we are going to study very subtle interactions using the NMR technique which aims precisely at the energy levels that result from spin–spin and spin–magnetic field interactions. Even if these effects are very small, they can be observed. Therefore, we have to consider more exact Hamiltonians. First, we have to introduce

- the interaction of our system with the electromagnetic field,
- then we will consider the influence of the electronic structure on the magnetic field acting on the nuclei

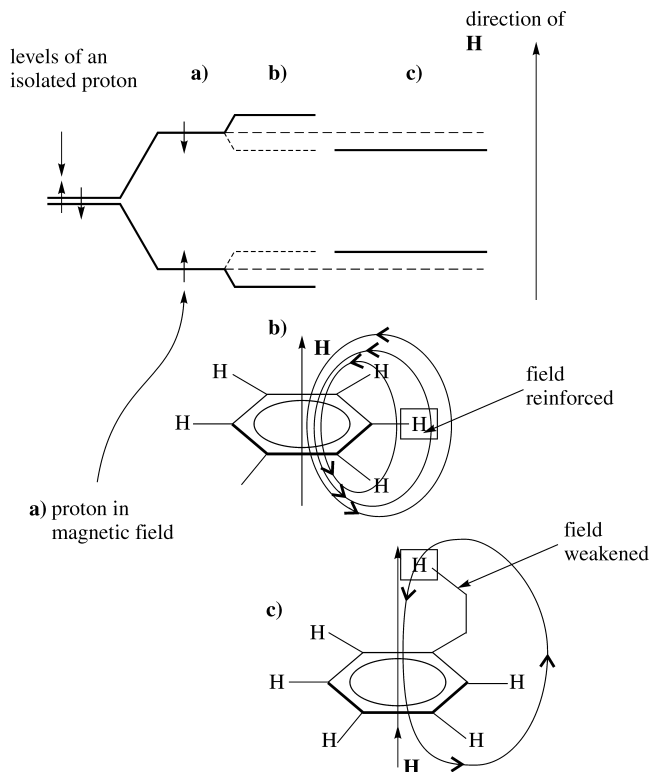


Fig. 12.11. Proton's shielding by the electronic structure. (a) The energy levels of an isolated proton in a magnetic field. (b) The energy levels of the proton of the benzene ring (no nuclear spin interaction is assumed). The most mobile π electrons of benzene (which may be treated as a conducting circular wire) move around the benzene ring in response to the external magnetic field (perpendicular to the ring) thus producing an induced magnetic field. The latter one (when considered along the ring six-fold axis) opposes the external magnetic field, but *at the position of the proton actually leads to an additional increasing of the magnetic field felt by the proton*. This is why the figure shows energy level difference increases due to the *electron shielding effect*. (c) The energy levels of another proton (located along the ring axis) in a similar molecule. This proton feels a local magnetic field that is decreased with respect to the external one (due to the induction effect).

- and finally, the nuclear magnetic moment interaction (“coupling”) will be considered.

12.8 HAMILTONIAN OF THE SYSTEM IN THE ELECTROMAGNETIC FIELD

The non-relativistic Hamiltonian⁵⁸ \hat{H} of the system of N particles (the j -th particle having mass m_j and charge q_j) moving in an external electromagnetic field with

⁵⁸To describe the interactions of the spin magnetic moments, this Hamiltonian will soon be supplemented by the relativistic terms from the Breit Hamiltonian (p. 131).

vector potential \mathbf{A} and scalar potential ϕ may be written as⁵⁹

$$\hat{H} = \sum_{j=1} \left[\frac{1}{2m_j} \left(\hat{\mathbf{p}}_j - \frac{q_j}{c} \mathbf{A}_j \right)^2 + q_j \phi_j \right] + \hat{V}, \quad (12.58)$$

where \hat{V} stands for the “internal” potential coming from the mutual interactions of the particles, and \mathbf{A}_j and ϕ_j denote the external vector⁶⁰ and scalar potentials \mathbf{A} and ϕ , respectively, calculated at the position of particle j .

12.8.1 CHOICE OF THE VECTOR AND SCALAR POTENTIALS

In Appendix G on p. 962 it is shown that there is a certain arbitrariness in the choice of both potentials, which leaves the physics of the system unchanged. If for a homogeneous magnetic field \mathbf{H} we choose the vector potential at the point indicated by $\mathbf{r} = (x, y, z)$ as (eq. (G.13)) $\mathbf{A}(\mathbf{r}) = \frac{1}{2}[\mathbf{H} \times \mathbf{r}]$, then, as shown in Appendix G, we will satisfy the Maxwell equations, and in addition obtain the commonly used relation (eq. (G.12)) $\text{div } \mathbf{A} \equiv \nabla \cdot \mathbf{A} = 0$, known as the *Coulombic gauge*. In this way the origin of the coordinate system ($\mathbf{r} = \mathbf{0}$) was chosen as the origin of the vector potential (which need not be a rule).

Because $\mathcal{E} = 0$ and \mathbf{A} is time-independent, $\phi = \text{const}$ (p. 962), which of course means also that $\phi_j = \text{const}$, and as an additive constant, it may simply be eliminated from the Hamiltonian (12.58).

12.8.2 REFINEMENT OF THE HAMILTONIAN

Let us assume the Born–Oppenheimer approximation (p. 229). Thus, the nuclei occupy some fixed positions in space, and in the electronic Hamiltonian (12.58) we have the electronic charges $q_j = -e$ and masses $m_j = m_0 = m$ (we skip the subscript 0 for the rest mass of the electron). Now, let us refine the Hamiltonian by adding the interaction of the particle magnetic moments (of the electrons and nuclei; the moments result from the orbital motion of the electrons as well as from the spin of each particle) with themselves and with the external magnetic field. We have, therefore, a refined Hamiltonian of the system [the particular terms of

⁵⁹To obtain this equation we may use eq. (3.33) as the starting point, which together with $E = mc^2$ gives with the accuracy of the first two terms in the expression $E = m_0 c^2 + \frac{p^2}{2m_0}$. In the electromagnetic field, after introducing the vector and scalar potentials for particle of charge q we have to replace E by $E - q\phi$, and \mathbf{p} by $(\mathbf{p} - \frac{q}{c}\mathbf{A})$. Then, after shifting the zero of the energy by $m_0 c^2$, the energy operator for a single particle reads as $\frac{1}{2m}(\hat{\mathbf{p}} - \frac{q}{c}\mathbf{A})^2 + q\phi$, where \mathbf{A} and ϕ are the values of the corresponding potentials at the position of the particle. For many particles we sum these contributions up and add the interparticle interaction potential (V). This is what we wanted to obtain (H. Hameka, “*Advanced Quantum Chemistry*”, Addison-Wesley Publishing Co., Reading, Massachusetts (1965), p. 40).

⁶⁰Note that the presence of the magnetic field (and therefore of \mathbf{A}) makes it to appear as if the charged particle moves faster on one side of the vector potential origin and slower on the opposite side.

the Hamiltonian correspond⁶¹ to the relevant terms of the Breit Hamiltonian⁶² (p. 131)]

$$\hat{\mathcal{H}} = \hat{H}_1 + \hat{\mathcal{H}}_2 + \hat{\mathcal{H}}_3 + \hat{\mathcal{H}}_4, \quad (12.59)$$

where (δ stands for the Dirac delta function, Appendix E, N is the number of electrons, and the spins have been replaced by the corresponding operators)

$$\hat{\mathcal{H}}_1 = \sum_{j=1}^N \frac{1}{2m} \left(\hat{\mathbf{p}}_j + \frac{e}{c} \mathbf{A}_j \right)^2 + \hat{V} + \hat{H}_{\text{SH}} + \hat{H}_{\text{IH}} + \hat{H}_{\text{LS}} + \hat{H}_{\text{SS}} + \hat{H}_{\text{LL}}, \quad (12.60)$$

$$\hat{\mathcal{H}}_2 = \gamma_{\text{el}} \sum_{j=1}^N \sum_A \gamma_A \left[\frac{\hat{\mathbf{s}}_j \cdot \hat{\mathbf{I}}_A}{r_{Aj}^3} - 3 \frac{(\hat{\mathbf{s}}_j \cdot \mathbf{r}_{Aj})(\hat{\mathbf{I}}_A \cdot \mathbf{r}_{Aj})}{r_{Aj}^5} \right], \quad (12.61)$$

$$\hat{\mathcal{H}}_3 = -\gamma_{\text{el}} \frac{8\pi}{3} \sum_{j=1}^N \sum_A \gamma_A \delta(\mathbf{r}_{Aj}) \hat{\mathbf{s}}_j \cdot \hat{\mathbf{I}}_A, \quad (12.62)$$

$$\hat{\mathcal{H}}_4 = \sum_{A < B} \gamma_A \gamma_B \left[\frac{\hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B}{R_{AB}^3} - 3 \frac{(\hat{\mathbf{I}}_A \cdot \mathbf{R}_{AB})(\hat{\mathbf{I}}_B \cdot \mathbf{R}_{AB})}{R_{AB}^5} \right], \quad (12.63)$$

where in the global coordinate system the internuclear distance means the length of the vector $\mathbf{R}_{AB} = \mathbf{R}_B - \mathbf{R}_A$, while the electron–nucleus distance (of the electron j with nucleus A) will be the length of $\mathbf{r}_{Aj} = \mathbf{r}_j - \mathbf{R}_A$. We have:

- In the term $\hat{\mathcal{H}}_1$, besides the kinetic energy operator in the external magnetic field [with vector potential \mathbf{A} , and the convention $\mathbf{A}_j \equiv \mathbf{A}(\mathbf{r}_j)$] given by $\sum_{j=1}^N \frac{1}{2m} (\hat{\mathbf{p}}_j + \frac{e}{c} \mathbf{A}_j)^2$, we have the Coulomb potential \hat{V} of the interaction of all the charged particles. Next, we have:
 - The interaction of the spin magnetic moments of the electrons (\hat{H}_{SH}) and of the nuclei (\hat{H}_{IH}) with the field \mathbf{H} . These terms come from the first part of the term \hat{H}_6 of the Breit Hamiltonian, and represent the simple Zeeman terms:

Pieter Zeeman (1865–1943), Dutch physicist, professor at the University of Amsterdam. He became interested in the influence of a magnetic field on molecular spectra and discovered a field-induced splitting of the absorption lines in 1896. He shared the Nobel Prize with Hendrik Lorentz “for their researches into the influence of magnetism upon radiation phenomena” in 1902. The Zeeman splitting of star spectra allows us to deter-



mine the value of the magnetic field that was on the star at the moment the light was emitted!

⁶¹All the terms used in the theory of magnetic susceptibilities and the Fermi contact term can be derived from classical electrodynamics.

⁶²Not all of them. As we will see later, the NMR experimental spectra are described by using, for each nucleus, what is known as the shielding constant (related to the shielding of the nucleus by the electron cloud) and the internuclear coupling constants. The shielding and coupling constants enter in a specific way into the energy expression. Only those terms are included in the Hamiltonian that give non-zero contributions to these quantities.

Zeeman term

- $\hat{\boldsymbol{\mu}} \cdot \mathbf{H}$, where $\hat{\boldsymbol{\mu}}$ is the magnetic moment operator of the corresponding particle. Why do we not have together with $\hat{H}_{\text{SH}} + \hat{H}_{\text{IH}}$ in $\hat{\mathcal{H}}_1$ the term \hat{H}_{LH} , i.e. the interaction of the electron orbital magnetic moment with the field? It would be so nice to have the full set of terms: the spin and the orbital magnetic moments interacting with the field. Everything is fine though, such a term is hidden in the mixed term resulting from $\frac{1}{2m}(\hat{\mathbf{p}}_j + \frac{e}{c}\mathbf{A}_j)^2$. Indeed, we get the corresponding Zeeman term from the transformation

$$\begin{aligned}\frac{e}{mc}\hat{\mathbf{p}}_j \cdot \mathbf{A}_j &= \frac{e}{mc}\mathbf{A}_j \cdot \hat{\mathbf{p}}_j = \frac{e}{2mc}(\mathbf{H} \times \mathbf{r}_j) \cdot \hat{\mathbf{p}}_j = \frac{e}{2mc}\mathbf{H} \cdot (\mathbf{r}_j \times \hat{\mathbf{p}}_j) \\ &= \frac{e}{2mc}\mathbf{H} \cdot \hat{\mathbf{L}}_j = -\mathbf{H} \cdot \left(-\frac{e}{2mc}\hat{\mathbf{L}}_j\right) = -\mathbf{H} \cdot \mathbf{M}_{\text{orb,el}}(j),\end{aligned}$$

where $\mathbf{M}_{\text{orb,el}}(j)$ is, according to the definition of eq. (12.53), the orbital magnetic moment of the electron j . Next, we have the terms

- the electronic spin–orbit terms (\hat{H}_{LS}), i.e. the corresponding magnetic dipole moment interactions; related to the term \hat{H}_3 in the Breit Hamiltonian.
- the electronic spin–spin terms (\hat{H}_{SS}), i.e. the corresponding spin magnetic moment interactions, related to the term \hat{H}_5 in the Breit Hamiltonian.
- the electronic orbit–orbit terms (\hat{H}_{LL}), i.e. the electronic orbital magnetic dipole interactions (corresponding to the term \hat{H}_2 in the Breit Hamiltonian).
- The terms $\hat{\mathcal{H}}_2, \hat{\mathcal{H}}_3, \hat{\mathcal{H}}_4$ (crucial for the NMR experiment) correspond to the magnetic “dipole–dipole” interaction involving *nuclear* spins (the term \hat{H}_5 of the Breit Hamiltonian). In more details these are the classical electronic spin–nuclear spin interaction ($\hat{\mathcal{H}}_2$), the corresponding Fermi contact term⁶³ ($\hat{\mathcal{H}}_3$) and the classical interaction of the nuclear spin magnetic dipoles ($\hat{\mathcal{H}}_4$), this time without the contact term, because the nuclei are kept at long distances by the chemical bond framework.⁶⁴

The magnetic dipole moment (of a nucleus or electron) “feels” the magnetic field acting on it through the vector potential \mathbf{A}_j at the particle’s position \mathbf{r}_j . This \mathbf{A}_j is composed of the external field vector potential $\frac{1}{2}[\mathbf{H} \times (\mathbf{r}_j - \mathbf{R})]$ (i.e. associated with the external magnetic field⁶⁵ \mathbf{H}), the individual vector potentials coming from the magnetic dipoles of the nuclei⁶⁶ $\sum_A \gamma_A \frac{\mathbf{I}_A \times \mathbf{r}_{Aj}}{r_{Aj}^3}$ (and having their origins on the individual nuclei) and the vector potential $\mathbf{A}_{\text{el}}(\mathbf{r}_j)$ coming from the orbital and spin

⁶³Let us take the example of the hydrogen atom in its ground state. Just note that the highest probability of finding the electron described by the orbital $1s$ is on the proton. The electron and the proton have spin magnetic moments that necessarily interact after they coincide. This effect is certainly something other than just the dipole–dipole interaction, which as usual describes the magnetic interaction for long distances. We have to have a correction for very short distances – this is the Fermi contact term.

⁶⁴And atomic electronic shell structure.

⁶⁵The vector \mathbf{R} indicates the origin of the external magnetic field \mathbf{H} vector potential from the global coordinate system (cf. Appendix G and the commentary there related to the choice of origin).

⁶⁶Recalling the force lines of a magnet, we see that the magnetic field vector \mathbf{H} produced by the nuclear magnetic moment $\gamma_A \mathbf{I}_A$ should reside within the plane of \mathbf{r}_{Aj} and $\gamma_A \mathbf{I}_A$. This means that \mathbf{A} has to be orthogonal to the plane. This is assured by \mathbf{A}_j proportional to $\gamma_A \mathbf{I}_A \times \mathbf{r}_{Aj}$.

magnetic moments of all the electrons

$$\mathbf{A}_j \equiv \mathbf{A}(\mathbf{r}_j) = \frac{1}{2}[\mathbf{H} \times \mathbf{r}_{0j}] + \sum_A \gamma_A \frac{\mathbf{I}_A \times \mathbf{r}_{Aj}}{r_{Aj}^3} + \mathbf{A}_{\text{el}}(\mathbf{r}_j), \quad (12.64)$$

where

$$\mathbf{r}_{0j} = \mathbf{r}_j - \mathbf{R}. \quad (12.65)$$

For closed-shell systems (the majority of molecules) the vector potential \mathbf{A}_{el} may be neglected, i.e. $\mathbf{A}_{\text{el}}(\mathbf{r}_j) \cong \mathbf{0}$, because the magnetic fields of the electrons cancel out for a closed-shell molecule (singlet state).

Rearranging terms

When such a vector potential \mathbf{A} is inserted into $\hat{\mathcal{H}}_1$ (just patiently make the square of the content of the parentheses) we immediately get

$$\hat{\mathcal{H}} = \hat{H}_0 + \hat{\mathcal{H}}^{(1)}, \quad (12.66)$$

where \hat{H}_0 is the usual non-relativistic Hamiltonian for the isolated system

$$\hat{H}_0 = - \sum_j \frac{\hbar^2}{2m} \Delta_j + \hat{V}, \quad (12.67)$$

$$\hat{\mathcal{H}}^{(1)} = \sum_k^{11} \hat{B}_k, \quad (12.68)$$

while a few minutes of a careful calligraphy leads to the result⁶⁷

$$\hat{B}_1 = \frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \frac{\hat{\mathbf{I}}_A \times \mathbf{r}_{Aj}}{r_{Aj}^3} \frac{\hat{\mathbf{I}}_B \times \mathbf{r}_{Bj}}{r_{Bj}^3}, \quad (12.69)$$

$$\hat{B}_2 = \frac{e^2}{8mc^2} \sum_j (\mathbf{H} \times \mathbf{r}_{0j}) \cdot (\mathbf{H} \times \mathbf{r}_{0j}), \quad (12.70)$$

$$\hat{B}_3 = -\frac{i\hbar e}{mc} \sum_A \sum_j \gamma_A \nabla_j \cdot \frac{\hat{\mathbf{I}}_A \times \mathbf{r}_{Aj}}{r_{Aj}^3}, \quad (12.71)$$

$$\hat{B}_4 = -\frac{i\hbar e}{2mc} \sum_j \nabla_j \cdot (\mathbf{H} \times \mathbf{r}_{0j}), \quad (12.72)$$

$$\hat{B}_5 = \frac{e^2}{2mc^2} \sum_A \sum_j \gamma_A (\mathbf{H} \times \mathbf{r}_{0j}) \cdot \frac{\hat{\mathbf{I}}_A \times \mathbf{r}_{Aj}}{r_{Aj}^3}, \quad (12.73)$$

$$\hat{B}_6 = \hat{\mathcal{H}}_2 = \gamma_{\text{el}} \sum_{j=1}^N \sum_A \gamma_A \left[\frac{\hat{\mathbf{s}}_j \cdot \hat{\mathbf{I}}_A}{r_{Aj}^3} - 3 \frac{(\hat{\mathbf{s}}_j \cdot \mathbf{r}_{Aj})(\hat{\mathbf{I}}_A \cdot \mathbf{r}_{Aj})}{r_{Aj}^5} \right], \quad (12.74)$$

⁶⁷The operators \hat{B}_3 and \hat{B}_4 contain the nabla (differentiation) operators. It is worth noting that this differentiation pertains to *everything on the right hand side of the nabla, including any function on which \hat{B}_3 and \hat{B}_4 operators will act.*

$$\hat{B}_7 = \hat{\mathcal{H}}_3 = -\gamma_{\text{el}} \frac{8\pi}{3} \sum_{j=1} \sum_A \gamma_A \delta(\mathbf{r}_{Aj}) \hat{\mathbf{s}}_j \cdot \hat{\mathbf{I}}_A, \quad (12.75)$$

$$\hat{B}_8 = \hat{H}_{\text{SH}} = -\gamma_{\text{el}} \sum_j \hat{\mathbf{s}}_j \cdot \mathbf{H}, \quad (12.76)$$

$$\hat{B}_9 = \hat{\mathcal{H}}_4 = \sum_{A < B} \gamma_A \gamma_B \left[\frac{\hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B}{R_{AB}^3} - 3 \frac{(\hat{\mathbf{I}}_A \cdot \mathbf{R}_{AB})(\hat{\mathbf{I}}_B \cdot \mathbf{R}_{AB})}{R_{AB}^5} \right], \quad (12.77)$$

$$\hat{B}_{10} = \hat{H}_{\text{IH}} = - \sum_A \gamma_A \hat{\mathbf{I}}_A \cdot \mathbf{H}, \quad (12.78)$$

$$\hat{B}_{11} = \hat{H}_{\text{LS}} + \hat{H}_{\text{SS}} + \hat{H}_{\text{LL}}. \quad (12.79)$$

We are just approaching the coupling of our theory with the NMR experiment. To this end, let us first define an empirical Hamiltonian, which serves in the NMR experiment to find what are known as the nuclear shielding constants and the spin-spin coupling constants. Then we will come back to the perturbation $\hat{\mathcal{H}}^{(1)}$.

12.9 EFFECTIVE NMR HAMILTONIAN

NMR spectroscopy⁶⁸ means recording the electromagnetic wave absorption by a system of interacting nuclear magnetic dipole moments.⁶⁹ It is important to note that the energy differences detectable by contemporary NMR equipment are of the order of 10^{-13} a.u., while the breaking of a chemical bond corresponds to about 10^{-1} a.u. This is why

all possible changes of the spin state of a system of nuclei do not change the chemical properties of the molecule. This is really what we could only dream of: we have something like observatory stations (the nuclear spins) that are able to detect tiny chemical bond details.

As will be seen in a moment, to reproduce NMR spectra we need an effective and rotation-averaged Hamiltonian that describes the interaction of the nuclear magnetic moments with the magnetic field and with themselves.

12.9.1 SIGNAL AVERAGING

NMR experiments usually pertain to long (many hours) recording of the radio-wave radiation coming from a liquid specimen. Therefore, we obtain a static (time-averaged) record, which involves various kinds of averaging:

⁶⁸The first successful experiment of this kind was described by E.M. Purcell, H.C. Torrey, R.V. Pound, *Phys. Rev.* 69 (1946) 37.

⁶⁹The wave lengths used in the NMR technique are of the order of meters (radio frequencies).

- over the rotations of any single molecule that contributes to the signal (we assume that each dipole keeps the same orientation in space when the molecule is rotating). These rotations can be free or restrained;
- over all the molecules present in the specimen;
- over the vibrations of the molecule (including internal rotations).

12.9.2 EMPIRICAL HAMILTONIAN

The effective NMR Hamiltonian contains some parameters that take into account the electronic cloud structure in which the nuclei are immersed. *These NMR parameters will represent our target.*

Now, let us proceed in this direction.

To interpret the NMR data, it is sufficient to consider an *effective* Hamiltonian (containing explicitly only the nuclear magnetic moments, the electron coordinates are absent and the electronic structure enters only implicitly through some interaction parameters). In the matrix notation we have

$$\hat{\mathcal{H}} = - \sum_A \gamma_A \mathbf{H}^T (\mathbf{1} - \boldsymbol{\sigma}_A) \mathbf{I}_A + \sum_{A < B} \gamma_A \gamma_B \{ \mathbf{I}_A^T (\mathbf{D}_{AB} + \mathbf{K}_{AB}) \mathbf{I}_B \}, \quad (12.80)$$

shielding
constants

where $\mathbf{I}_C \equiv (I_{C,x}, I_{C,y}, I_{C,z})^T$ stands for the spin angular momentum of the nucleus C , while $\boldsymbol{\sigma}_A$, \mathbf{D}_{AB} , \mathbf{K}_{AB} denote the symmetric square matrices of dimension three (*tensors*):

- $\boldsymbol{\sigma}_A$ is a *shielding constant* tensor of the nucleus A . Due to this shielding, nucleus A feels a *local field* $\mathbf{H}_{\text{loc}} = (\mathbf{1} - \boldsymbol{\sigma}_A) \mathbf{H} = \mathbf{H} - \boldsymbol{\sigma}_A \mathbf{H}$ instead of the external field \mathbf{H} applied (due to the tensor character of $\boldsymbol{\sigma}_A$ the vectors \mathbf{H}_{loc} and \mathbf{H} may differ in their length and direction). The formula assumes that the shielding is proportional to the external magnetic field intensity that causes the shielding. Thus, the first term in the Hamiltonian $\hat{\mathcal{H}}$ may also be written as $-\sum_A \gamma_A \mathbf{H}_{\text{loc}}^T \mathbf{I}_A$.
- \mathbf{D}_{AB} is the 3×3 matrix describing the (direct) *dipole–dipole interaction through space* defined above.
- \mathbf{K}_{AB} is also a 3×3 matrix that takes into account that two magnetic dipoles interact additionally through the framework of the chemical bonds or hydrogen bonds that separate them. This is known as the *reduced spin–spin intermediate coupling tensor*.

local field

Without electrons...

Let us imagine, just for fun, removing all the electrons from the molecule (and keep them safely in a drawer), while the nuclei still reside in their fixed positions in space. The Hamiltonian would consist of two types of term:

- the *Zeeman term*: interaction of the nuclear magnetic moments with the external electric field (the nuclear analogue of the first term in \hat{H}_6 of the Breit Hamiltonian, p. 131) $-\sum_A \mathbf{H} \cdot \hat{\mathbf{M}}_A = -\sum_A \gamma_A \mathbf{H} \cdot \hat{\mathbf{I}}_A$;
- the “through space” dipole–dipole nuclear magnetic moment interaction (the nuclear analogue of the \hat{H}_5 term in the Breit Hamiltonian) $\sum_{A < B} \gamma_A \gamma_B (\hat{\mathbf{I}}_A \cdot$

$D_{AB}\hat{\mathbf{I}}_B\}$:

$$D_{AB} = \frac{\mathbf{i} \cdot \mathbf{j}}{R_{AB}^3} - 3 \frac{(\mathbf{i} \cdot \mathbf{R}_{AB})(\mathbf{j} \cdot \mathbf{R}_{AB})}{R_{AB}^5},$$

where \mathbf{i}, \mathbf{j} denote the unit vectors along the x, y, z axes, e.g.,

$$(D_{AB})_{xx} = \frac{1}{R_{AB}^3} - 3 \frac{(R_{AB,x})^2}{R_{AB}^5}, \quad (D_{AB})_{xy} = -3 \frac{R_{AB,x}R_{AB,y}}{R_{AB}^5}, \quad \text{etc.}$$

with \mathbf{R}_{AB} denoting the vector separating nucleus B from nucleus A (of length R_{AB}).

Rotations average out the dipole–dipole interaction

What would happen if we rotated the molecule? In the theory of NMR, there are a lot of notions stemming from classical electrodynamics. In the isolated molecule the total angular momentum has to be conserved (this follows from the isotropic properties of space). The total angular momentum comes, not only from the particles' orbital motion, but also from their spin contributions. The empirical (non-fundamental) conservation law pertains to the total spin angular momentum alone (cf. p. 68), as well as the individual spins separately. The spin magnetic moments are oriented in space and this orientation results from the history of the molecule and may be different in each molecule of the substance. These spin states are non-stationary. The *stationary states correspond to some definite values of the square of the total spin of the nuclei and of the spin projection on a chosen axis*. According to quantum mechanics (Chapter 1), only these values are to be measured. For example, in the hydrogen molecule there are two stationary nuclear spin states: one with parallel spins (ortho-hydrogen) and the other with antiparallel (para-hydrogen). Then we may assume that the hydrogen molecule has two “nuclear gyroscopes” that keep pointing them in the same direction in space when the molecule rotates (Fig. 12.12).

Let us see what will happen if we average the interaction of two magnetic dipole moments (the formula for the interaction of two dipoles will be derived in Chapter 13, p. 701):

$$E_{\text{dip-dip}} = \frac{\mathbf{M}_A \cdot \mathbf{M}_B}{R_{AB}^3} - 3 \frac{(\mathbf{M}_A \cdot \mathbf{R}_{AB})(\mathbf{M}_B \cdot \mathbf{R}_{AB})}{R_{AB}^5}.$$

Assume (without losing the generality of the problem) that \mathbf{M}_A resides at the origin of a polar coordinate system and has a constant direction along the z axis, while the dipole \mathbf{M}_B just moves on the sphere of the radius R_{AB} around \mathbf{M}_A (all orientations are equally probable), the \mathbf{M}_B vector preserving the same direction in space ($\theta, \phi) = (u, 0)$ all the time. Now, let us calculate the average value of $E_{\text{dip-dip}}$ with respect to all possible positions of \mathbf{M}_B on the sphere:

$$\begin{aligned} \bar{E}_{\text{dip-dip}} &= \frac{1}{4\pi} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi E_{\text{dip-dip}} \\ &= \frac{1}{4\pi} \int_0^\pi d\theta \sin \theta \end{aligned}$$

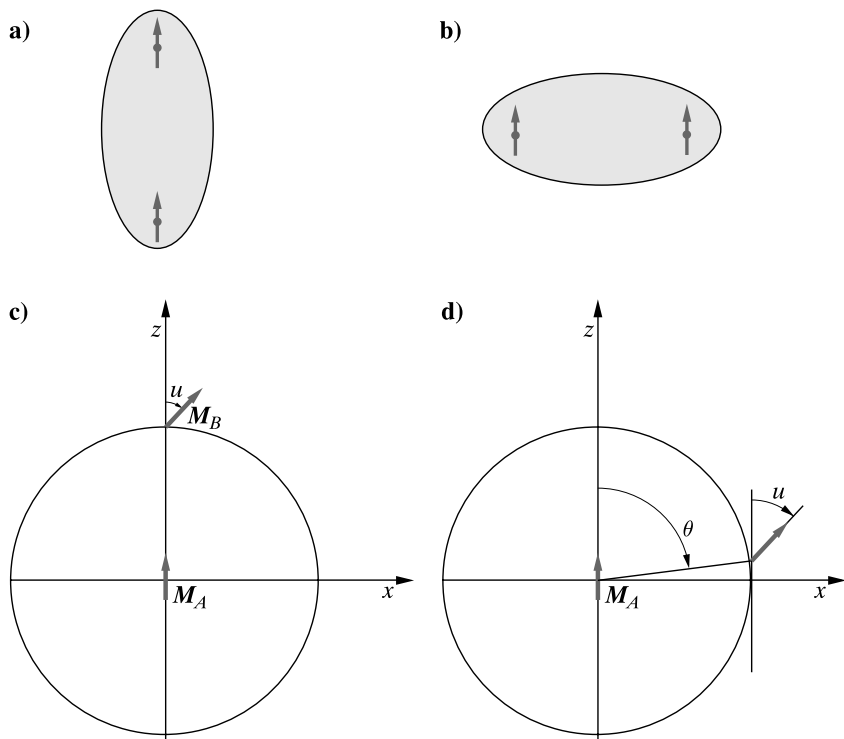


Fig. 12.12. Rotation of a molecule and the nuclear magnetic moments. Fig. (a) shows the orientation of the nuclear magnetic moments in the orthohydrogen at the vertical configuration of the nuclei. Fig. (b) shows the same, but the molecule is oriented horizontally. In the theory of NMR, we assume (in a classical way), that the motion of the molecule does not influence the orientation of both nuclear magnetic moments (c) averaging the dipole-dipole interaction over all possible orientations. Let us immobilize the magnetic moment M_A along the z axis, the magnetic moment M_B will move on the sphere of radius 1 both moments still keeping the same direction in space $(\theta, \phi) = (u, 0)$. Fig. (d) shows one of such configurations. Averaging over all possible orientations gives zero (see the text).

$$\begin{aligned}
 & \times \int_0^{2\pi} d\phi \left[\frac{1}{R_{AB}^3} \mathbf{M}_A \cdot \mathbf{M}_B - \frac{3}{R_{AB}^5} (\mathbf{M}_A \cdot \mathbf{R}_{AB})(\mathbf{M}_B \cdot \mathbf{R}_{AB}) \right] \\
 &= \frac{M_A M_B}{4\pi R_{AB}^3} \int_0^\pi d\theta \sin \theta \int_0^{2\pi} d\phi [\cos u - 3 \cos \theta \cos(\theta - u)] \\
 &= \frac{M_A M_B}{2R_{AB}^3} \int_0^\pi d\theta \sin \theta [\cos u - 3 \cos \theta \cos(\theta - u)] \\
 &= \frac{M_A M_B}{R_{AB}^3} \left\{ \cos u - \frac{3}{2} \int_0^\pi d\theta \sin \theta \cos \theta [\cos \theta \cos u + \sin \theta \sin u] \right\} \\
 &= \frac{M_A M_B}{R_{AB}^3} \left\{ \cos u - \frac{3}{2} \left[\cos u \cdot \frac{2}{3} + \sin u \cdot 0 \right] \right\} = 0. \quad (12.81)
 \end{aligned}$$

Thus, the averaging gave 0 irrespective of the radius R_{AB} and of the angle u between the two dipoles. This result was obtained when assuming the orientations of both dipoles do not change (the above mentioned “gyroscopes”) and that all angles θ and ϕ are equally probable.

Averaging over rotations

An NMR experiment requires long recording times. This means that each molecule, when rotating freely (gas or liquid⁷⁰) with respect to the NMR apparatus, acquires all possible orientations with equal probability. The equipment will detect an averaged signal. This is why the proposed effective Hamiltonian has to be averaged over the rotations. As we have shown, such an averaging causes the mean dipole–dipole interaction (containing \mathbf{D}_{AB}) to be equal to zero. If we assume that the external magnetic field is along the z axis, then the averaged Hamiltonian reads as

$$\hat{\mathcal{H}}_{\text{av}} = - \sum_A \gamma_A (1 - \sigma_A) H_z \hat{I}_{A,z} + \sum_{A < B} \gamma_A \gamma_B K_{AB} (\hat{\mathbf{I}}_A \cdot \hat{\mathbf{I}}_B), \quad (12.82)$$

where $\sigma_A = \frac{1}{3}(\sigma_{A,xx} + \sigma_{A,yy} + \sigma_{A,zz}) = \frac{1}{3} \text{Tr } \boldsymbol{\sigma}_A$, with $K_{AB} = \frac{1}{3} \text{Tr } \mathbf{K}_{AB}$.

This Hamiltonian is at the basis of NMR spectra interpretation. An experimentalist adjusts σ_A for all the magnetic nuclei and K_{AB} for all their interactions, in order to reproduce the observed spectrum. Any theory of NMR spectra should explain the values of these parameters.

Adding the electrons – why the nuclear spin interaction does not average out to zero

We know already why \mathbf{D}_{AB} averages out to zero, but why is this not true for \mathbf{K}_{AB} ?

Ramsey and Purcell⁷¹ explained this by what is known as the spin induction mechanism described in Fig. 12.13. Spin induction results in the averaging of \mathbf{K}_{AB} and the spin–spin configurations have different weights than in the averaging of \mathbf{D}_{AB} . This effect is due to the chemical bonds, because it makes a difference if the correlating electrons have their spins oriented parallel or perpendicular to the bond line.

Where does such an effect appear in quantum chemistry? One of the main candidates may be the term \hat{H}_3 (the Fermi contact term in the Breit Hamiltonian, p. 131) which couples the orbital motion of the electrons with their spin magnetic

⁷⁰This is not the case in the solid state.

⁷¹N.F. Ramsey, E.M. Purcell, *Phys. Rev.* 85 (1952) 143.

Norman F. Ramsey (born in 1915), American physicist, professor at the University of Illinois and Columbia University, then from 1947 at the Harvard University. He is first of all an outstanding experimentalist in the domain of NMR measurements in molecular jets, but his "hobby" is theoretical physics. Ramsey carried out the first accurate measurement of the neutron magnetic moment and gave a lower bound theoretical estimation to its dipole moment. In 1989 he received the Nobel prize "for the invention of the separated oscillatory fields



method and its use in the hydrogen maser and other atomic clocks."

Edwards Mills Purcell (1912–1997), American physicist, professor at the Massachusetts Institute of Technology and Harvard University. His main domains were relaxation phenomena and magnetic properties in low temperatures. He received the Nobel prize together with Felix Bloch "for their development of new methods for nuclear magnetic precision measurements and discoveries in connection therewith" In 1952.



moments. This is a relativistic effect, hence it is very small and therefore the rotational averaging results in only a small value for K_{AB} .

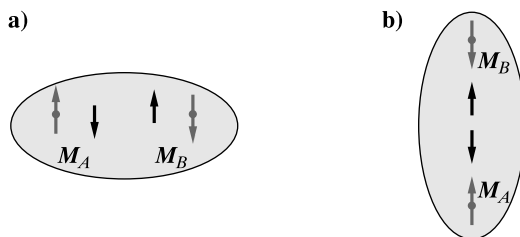


Fig. 12.13. The nuclear spin–spin coupling (Fermi contact) mechanism through chemical bond AB . The electrons repel each other and therefore correlate their motion (cf. p. 515). This is why, when one of them is close to nucleus A , the second prefers to run off to nucleus B . For some nuclei the electron–nucleus interaction of the magnetic dipole moments of A , and of the first electron near the last, will exhibit a tendency (i.e. the corresponding energy will be lower than in the opposite case) to have a spin antiparallel to the spin of A – this is what happens for protons and electrons. The second electron, close to B , must have an opposite spin to its partner, and therefore will exhibit a tendency to have its spin *the same as that of nucleus A*. We may say that the electron exposes the spin of nucleus A right at the position of the nucleus B . Such a mechanism gives a much stronger magnetic dipole interaction than that through empty space. Fig. (a) shows a favourable configuration of nuclear and electron spins, all perpendicular to the bond, Fig. (b) shows the same situation after the molecule is rotated by 90° . The electronic correlation energy will obviously differ in these two orientations of the molecule, and this results in different averaging than in the case of the interaction through space.

12.9.3 NUCLEAR SPIN ENERGY LEVELS

From calculating the mean value of the Hamiltonian (12.82), we obtain the energy of the nuclear spins in the magnetic field

$$E = - \sum_A (1 - \sigma_A) \gamma_A H m_{I,A} \hbar + \sum_{A < B} \gamma_A \gamma_B K_{AB} \langle \hat{I}_A \cdot \hat{I}_B \rangle,$$

where $\langle \hat{I}_A \cdot \hat{I}_B \rangle$ is the mean value of the scalar product of the two spins calculated by using their spin functions. This expression can be simplified by the following transformation

$$\begin{aligned} E &= - \sum_A (1 - \sigma_A) \gamma_A H m_{I,A} \hbar + \sum_{A < B} \gamma_A \gamma_B K_{AB} \langle \hat{I}_{A,x} \hat{I}_{B,x} + \hat{I}_{A,y} \hat{I}_{B,y} + \hat{I}_{A,z} \hat{I}_{B,z} \rangle \\ &= - \sum_A (1 - \sigma_A) \gamma_A H m_{I,A} \hbar + \sum_{A < B} \gamma_A \gamma_B K_{AB} (0 \cdot 0 + 0 \cdot 0 + \hbar^2 m_{I,A} m_{I,B}), \end{aligned}$$

because the mean values of $\hat{I}_{C,x}$ and $\hat{I}_{C,y}$ calculated for the spin functions of nucleus C both equal 0 (for the α or β functions describing a nucleus with $I_C = \frac{1}{2}$, see Chapter 1, p. 30). Therefore, the energy becomes a function of the magnetic spin quantum numbers $m_{I,C}$ for all the nuclei with a non-zero spin I_C

$$E(m_{I,A}, m_{I,B}, \dots) = -\hbar H \sum_A (1 - \sigma_A) \gamma_A m_{I,A} + \sum_{A < B} \hbar J_{AB} m_{I,A} m_{I,B}, \quad (12.83)$$

coupling
constant

where the commonly used nuclear spin–spin *coupling constant* is defined as

$$J_{AB} \equiv \frac{\hbar}{2\pi} \gamma_A \gamma_B K_{AB}. \quad (12.84)$$

Note that since $\hbar J_{AB}$ has the dimension of the energy, then J_{AB} itself is a frequency and may be expressed in Hz.

Due to the presence of the rest of the molecule (electron shielding) the Larmor frequency $\nu_A = \frac{H\gamma_A}{2\pi} (1 - \sigma_A)$ is changed by $-\sigma_A \frac{H\gamma_A}{2\pi}$ with respect to the Larmor frequency $\frac{H\gamma_A}{2\pi}$ for an isolated proton. Such changes are usually expressed (as “ppm”, i.e. “parts per million”⁷²) by the *chemical shift* δ_A

chemical shift

$$\delta_A = \frac{\nu_A - \nu_{\text{ref}}}{\nu_{\text{ref}}} \cdot 10^6 = \frac{\sigma_{\text{ref}} - \sigma_A}{\sigma_{\text{ref}}} \cdot 10^6, \quad (12.85)$$

where ν_{ref} is the Larmor frequency for a reference nucleus [for protons this means by convention the proton Larmor frequency in tetramethylsilane, $\text{Si}(\text{CH}_3)_4$]. The chemical shifts (unlike the Larmor frequencies) are independent of the magnetic field applied.

Example 3. The carbon nucleus in an external magnetic field

Let us consider a single carbon ^{13}C nucleus (spin quantum number $I_C = \frac{1}{2}$) in a molecule.

⁷²This means the chemical shift (unitless quantity) has to be multiplied by 10^{-6} to obtain $\frac{\nu_A - \nu_{\text{ref}}}{\nu_{\text{ref}}}$.

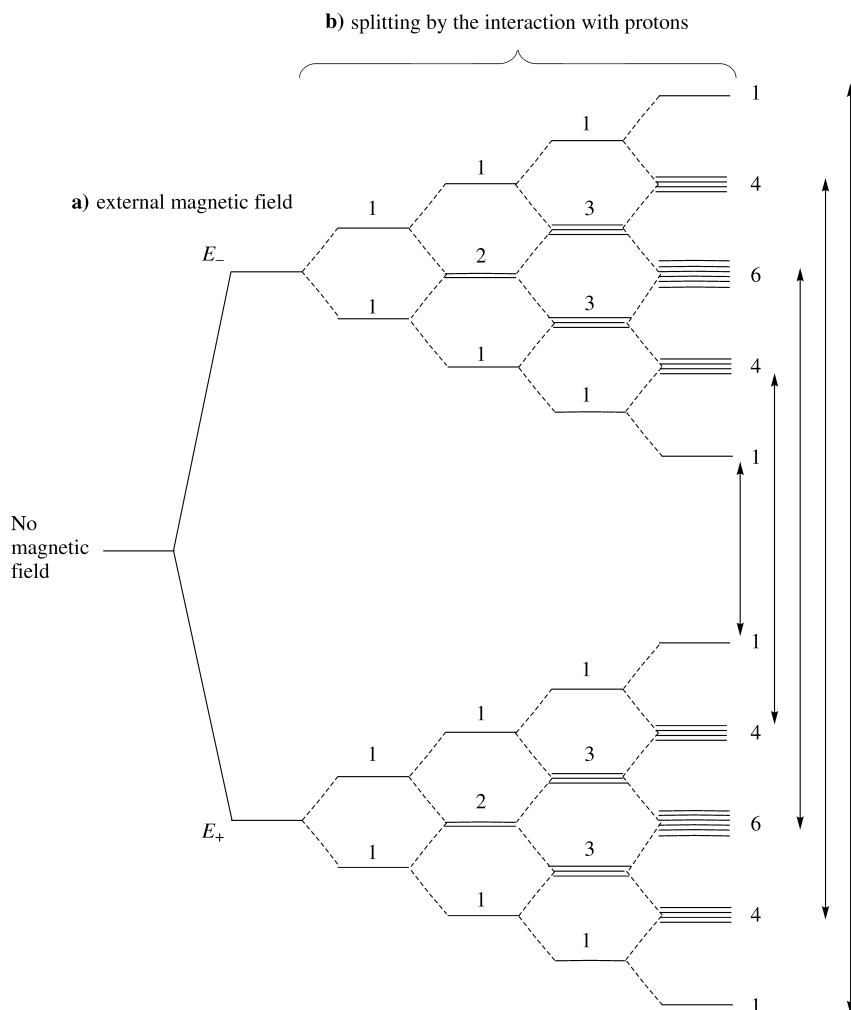


Fig. 12.14. The energy levels of the ^{13}C magnetic moment in the methane molecule and in an external magnetic field. (a) The spin energy levels of the ^{13}C atom in an external magnetic field; (b) additional interaction of the ^{13}C spin with the four equivalent proton magnetic moments switched on. As we can see the energy levels in each branch follow the Pascal triangle rule. The splits within the branch come from the coupling of the nuclei and are field-independent. The E_+ and E_- energies are field-dependent: increasing field means a tuning of the separation between the energy levels. The resonance takes place when the field-dependent energy difference matches the energy of the electromagnetic field quanta. The NMR selection rule means that only the transitions indicated take place. Since the energy split due to the coupling of the nuclei is very small, the levels E_+ are equally occupied and therefore the NMR intensities satisfy the ratio: 1 : 4 : 6 : 4 : 1.

As seen from eq. (12.83) such a nucleus in magnetic field H has two energy levels (for $m_{I,C} = \pm \frac{1}{2}$, Fig. 12.14.a)

$$E(m_{I,C}) = -\hbar H(1 - \sigma_C)\gamma_C m_{I,C},$$

where the shielding constant σ_C characterizes the vicinity of the nucleus. For the isolated nucleus $\sigma_C = 0$.

Example 4. The methane molecule $^{13}\text{CH}_4$ in magnetic field H

This time there is an additional magnetic field coming from four equivalent protons, each having $I_H = \frac{1}{2}$. The energy levels of the carbon magnetic spin result from the magnetic field and from the $m_{I,H}$'s of the protons according to eq. (12.83), Fig. 12.14. The resonance of the ^{13}C nucleus means a transition between energy levels that correspond to $m_{I,C} = \pm \frac{1}{2}$ with all the m_{I,H_i} being constant.⁷³ Thus, the lower level corresponds to

$$\begin{aligned} E_+(m_{I,H_1}, m_{I,H_2}, m_{I,H_3}, m_{I,H_4}) \\ = -\frac{\hbar}{2}H(1 - \sigma_C)\gamma_C + \frac{\hbar^1}{2}J_{CH}(m_{I,H_1} + m_{I,H_2} + m_{I,H_3} + m_{I,H_4}), \end{aligned}$$

and at the higher level we have the energy

$$\begin{aligned} E_-(m_{I,H_1}, m_{I,H_2}, m_{I,H_3}, m_{I,H_4}) \\ = \frac{\hbar}{2}H(1 - \sigma_C)\gamma_C - \frac{\hbar^1}{2}J_{CH}(m_{I,H_1} + m_{I,H_2} + m_{I,H_3} + m_{I,H_4}). \end{aligned}$$

Since $m_{I,H_i} = \pm \frac{1}{2}$ then each of the levels E_{\pm} will be split into 5 levels, Fig. 12.14:

- a non-degenerate level arising from all $m_{I,H_i} = \frac{1}{2}$,
- a quadruply degenerate level that comes from all $m_{I,H_i} = \frac{1}{2}$, except one equal to $-\frac{1}{2}$ (there are four positions of this one),
- a sextuply degenerate level that results from two $m_{I,H_i} = \frac{1}{2}$ and two $m_{I,H_i} = -\frac{1}{2}$ (six ways of achieving this),
- a quadruply degenerate level that comes from all $m_{I,H_i} = -\frac{1}{2}$, except one that equals $\frac{1}{2}$ (there are four positions of this one),
- a non-degenerate level arising from all $m_{I,H_i} = -\frac{1}{2}$.

12.10 THE RAMSEY THEORY OF THE NMR CHEMICAL SHIFT

An external magnetic field H or/and the magnetic field produced by the nuclei magnetic dipole moments $\mathbf{M}_1, \mathbf{M}_2, \mathbf{M}_3, \dots$ certainly represent an extremely weak perturbation to the energy of a molecule, and therefore, the changes they induce in the molecule are suitable for perturbational methods.

We decide to apply the theory through the second order. Such an effect is composed of two parts:

- the first-order correction (*the diamagnetic contribution*),
- the second-order correction (*the paramagnetic contribution*).

⁷³The NMR selection rule for a given nucleus says that the single nucleus undergoes a flip.

The corresponding energy change due to the perturbation $\hat{\mathcal{H}}^{(1)}$ from eq. (12.68) (prime means that $k = 0$, i.e. the ground state is excluded from the summation)

$$\Delta E = E_0^{(1)} + E_0^{(2)} = \langle \psi_0^{(0)} | \hat{\mathcal{H}}^{(1)} | \psi_0^{(0)} \rangle + \sum_k' \frac{\langle \psi_0^{(0)} | \hat{\mathcal{H}}^{(1)} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{\mathcal{H}}^{(1)} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}}. \quad (12.86)$$

12.10.1 SHIELDING CONSTANTS

In the Hamiltonian (12.82) the shielding constants occur in the term $\mathbf{I}_A \cdot \mathbf{H}$. The perturbation operator $\hat{H}^{(1)}$ contains a lot of terms, but most of them, when inserted into the above formula, are unable to produce terms that behave like $\mathbf{I}_A \cdot \mathbf{H}$. Only some very particular terms could produce such a dot product dependence. A minute of reflection leads directly to \hat{B}_3 , \hat{B}_4 , \hat{B}_5 and \hat{B}_{10} as the only terms of the Hamiltonian that have any chance of producing the dot product form.⁷⁴ Therefore, using the definition of the reduced resolvent \hat{R}_0 of eq. (10.64) we have⁷⁵

$$\begin{aligned} \Delta E = E_0^{(1)} + E_0^{(2)} &= \langle \psi_0^{(0)} | (\hat{B}_{10} + \hat{B}_5) | \psi_0^{(0)} \rangle \\ &+ \langle \psi_0^{(0)} | (\hat{B}_3 \hat{R}_0 \hat{B}_4 + \hat{B}_4 \hat{R}_0 \hat{B}_3) | \psi_0^{(0)} \rangle. \end{aligned} \quad (12.87)$$

After averaging the formula over rotations and extracting the proper term (details given in Appendix W, p. 1032) we obtain as the shielding constant of the nucleus A

$$\begin{aligned} \sigma_A = \frac{e^2}{3mc^2} &\left\langle \psi_0^{(0)} \left| \sum_j (\mathbf{r}_{0j} \cdot \mathbf{r}_{Aj}) \frac{1}{r_{Aj}^3} \psi_0^{(0)} \right. \right\rangle - \frac{e^2}{6m^2c^2} \left\langle \psi_0^{(0)} \left| \left[\left(\sum_j \frac{\hat{\mathbf{L}}_{Aj}}{r_{Aj}^3} \right) \hat{R}_0 \left(\sum_j \hat{\mathbf{L}}_{0j} \right) \right. \right. \right. \\ &\left. \left. \left. + \left(\sum_j \hat{\mathbf{L}}_{0j} \right) \hat{R}_0 \left(\sum_j \frac{\hat{\mathbf{L}}_{Aj}}{r_{Aj}^3} \right) \right] \psi_0^{(0)} \right. \right\rangle, \end{aligned} \quad (12.88)$$

⁷⁴There is an elegant way to single out the only necessary B_i 's that give a contribution to the energy proportional to the product $x_i x_j$ (no higher terms included), where x_i and x_j stand for some components of the magnetic field intensity \mathbf{H} or of the nuclear spin \mathbf{I}_A 's (that cause perturbation of the molecule). As to the first-order correction ("diamagnetic") we calculate the second derivative $(\frac{\partial^2 \hat{\mathcal{H}}^{(1)}}{\partial x_i \partial x_j})_{\mathbf{H}=\mathbf{0}, \mathbf{I}_i=\mathbf{0}}$ of the Hamiltonian $\hat{\mathcal{H}}^{(1)}$ with respect to the components of \mathbf{H} or \mathbf{I}_A , afterwards inserting $\mathbf{H} = \mathbf{0}$ and $\mathbf{I}_A = \mathbf{0}$ (i.e. calculating the derivative at zero perturbation). Then the diamagnetic correction to the energy is $\langle \psi_0^{(0)} | (\frac{\partial^2 \hat{\mathcal{H}}^{(1)}}{\partial x_i \partial x_j})_{\mathbf{H}=\mathbf{0}, \mathbf{I}_i=\mathbf{0}} | \psi_0^{(0)} \rangle$. As to the second-order correction ("paramagnetic"), we calculate the first derivatives: $(\frac{\partial \hat{\mathcal{H}}^{(1)}}{\partial x_i})_{\mathbf{H}=\mathbf{0}, \mathbf{I}_i=\mathbf{0}}$ and $(\frac{\partial \hat{\mathcal{H}}^{(1)}}{\partial x_j})_{\mathbf{H}=\mathbf{0}, \mathbf{I}_i=\mathbf{0}}$ and, therefore, the contribution to the energy is

$$\sum_k' \frac{\langle \psi_0^{(0)} | (\frac{\partial \hat{\mathcal{H}}^{(1)}}{\partial x_i})_{\mathbf{H}=\mathbf{0}, \mathbf{I}_i=\mathbf{0}} | \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | (\frac{\partial \hat{\mathcal{H}}^{(1)}}{\partial x_j})_{\mathbf{H}=\mathbf{0}, \mathbf{I}_i=\mathbf{0}} | \psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}}.$$

⁷⁵Note that whenever the reduced resolvent appears in a formula, infinite summation over unperturbed states is involved.

where

$$\hat{\mathbf{L}}_{Aj} = -i\hbar(\mathbf{r}_{Aj} \times \nabla_j) \quad (12.89)$$

and

$$\hat{\mathbf{L}}_{0j} = -i\hbar(\mathbf{r}_{0j} \times \nabla_j) \quad (12.90)$$

stand for the angular momenta operators for the electron j calculated with respect to the position of nucleus A and with respect the origin of vector potential A , respectively.

12.10.2 DIAMAGNETIC AND PARAMAGNETIC CONTRIBUTIONS

The result (12.88) has been obtained (apparently) in two parts:

$$\sigma_A = \sigma_A^{\text{dia}} + \sigma_A^{\text{para}}, \quad (12.91)$$

called the *diamagnetic contribution*

$$\sigma_A^{\text{dia}} = \frac{e^2}{3mc^2} \left\langle \psi_0^{(0)} \left| \sum_j (\mathbf{r}_{0j} \cdot \mathbf{r}_{Aj}) \frac{1}{r_{Aj}^3} \psi_0^{(0)} \right. \right\rangle$$

and the *paramagnetic contribution*

$$\begin{aligned} \sigma_A^{\text{para}} = & -\frac{e^2}{6m^2c^2} \left\langle \psi_0^{(0)} \left| \left[\left(\sum_j \frac{\hat{\mathbf{L}}_{Aj}}{r_{Aj}^3} \right) \hat{R}_0 \left(\sum_j \hat{\mathbf{L}}_{0j} \right) \right. \right. \right. \\ & \left. \left. + \left(\sum_j \hat{\mathbf{L}}_{0j} \right) \hat{R}_0 \left(\sum_j \frac{\hat{\mathbf{L}}_{Aj}}{r_{Aj}^3} \right) \right] \psi_0^{(0)} \right. \right\rangle. \end{aligned}$$

Each of these contributions looks suspicious. Indeed, the diamagnetic contribution explicitly depends on the choice of origin \mathbf{R} of vector potential A through $\mathbf{r}_{0j} = \mathbf{r}_j - \mathbf{R}$, see (12.65). Similarly, the paramagnetic contribution also depends on choice through $\hat{\mathbf{L}}_{0j}$ and (12.65). We have already stressed the *practical* importance of the choice of \mathbf{R} in Appendix G. Since both contributions depend on the choice, they separately cannot have any physical significance.

Is it possible that the *sum* of the two contributions is invariant with respect to choice of \mathbf{R} ? Yes, it is! The invariance has fortunately been proved.⁷⁶ This is good, because any measurable quantity cannot depend on an arbitrary choice of the origin of the coordinate system.

12.11 THE RAMSEY THEORY OF NMR SPIN-SPIN COUPLING CONSTANTS

We will apply the same philosophy as that used for shielding constants (or, equivalently, of the NMR chemical shift) to calculate the nuclear coupling constant.

⁷⁶A. Abragam, "The Principles of Nuclear Magnetism", Clarendon Press, Oxford (1961).

Taking into account the Hamiltonian $\hat{\mathcal{H}}^{(1)}$ from eq. (12.68), we note that the only terms in $\hat{\mathcal{H}}^{(1)}$ that have the chance to contribute to the NMR coupling constants (see eq. (12.83)) are

$$\Delta E = E_0^{(1)} + E_0^{(2)} = \langle \psi_0^{(0)} | (\hat{B}_1 + \hat{B}_9) \psi_0^{(0)} \rangle \quad (12.92)$$

$$+ \sum_k \frac{\langle \psi_0^{(0)} | (\hat{B}_3 + \hat{B}_6 + \hat{B}_7) \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | (\hat{B}_3 + \hat{B}_6 + \hat{B}_7) \psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}} \\ = E_{\text{dia}} + E_{\text{para}}, \quad (12.93)$$

because we are looking for terms that could result in the scalar product of the nuclear magnetic moments. The first term is the diamagnetic contribution (E_{dia}), the sum is the paramagnetic contribution (E_{para}).

12.11.1 DIAMAGNETIC CONTRIBUTIONS

There are two diamagnetic contributions in the total diamagnetic effect $\langle \psi_0^{(0)} | (\hat{B}_1 + \hat{B}_9) \psi_0^{(0)} \rangle$:

- The $\langle \psi_0^{(0)} | \hat{B}_9 \psi_0^{(0)} \rangle$ term simply represents the $\sum_{A < B} \gamma_A \gamma_B \mathbf{I}_A^T \mathbf{D}_{AB} \mathbf{I}_B$ contribution of eq. (12.80), i.e. the *direct* (“through space”) *nuclear spin–spin interaction*. This calculation does not require anything except summation over spin–spin terms. However, *as has been shown, averaging over free rotations of the molecule in the specimen renders this term equal to zero.*
- The $\langle \psi_0^{(0)} | \hat{B}_1 \psi_0^{(0)} \rangle$ term can be transformed in the following way:

direct spin–spin
contribution

$$\langle \psi_0^{(0)} | \hat{B}_1 \psi_0^{(0)} \rangle = \left\langle \psi_0^{(0)} \left| \left(\frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \frac{\mathbf{I}_A \times \mathbf{r}_{Aj}}{r_{Aj}^3} \frac{\mathbf{I}_B \times \mathbf{r}_{Bj}}{r_{Bj}^3} \right) \psi_0^{(0)} \right| \right\rangle \\ = \frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \left\langle \psi_0^{(0)} \left| \frac{(\mathbf{I}_A \times \mathbf{r}_{Aj}) \cdot (\mathbf{I}_B \times \mathbf{r}_{Bj})}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right| \right\rangle.$$

Now, note that $(\mathbf{A} \times \mathbf{B}) \cdot \mathbf{C} = \mathbf{A} \cdot (\mathbf{B} \times \mathbf{C})$. Taking $\mathbf{A} = \mathbf{I}_A$, $\mathbf{B} = \mathbf{r}_{Aj}$, $\mathbf{C} = \mathbf{I}_B \times \mathbf{r}_{Bj}$ we first have the following

$$\langle \psi_0^{(0)} | \hat{B}_1 \psi_0^{(0)} \rangle = \frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \mathbf{I}_A \cdot \left\langle \psi_0^{(0)} \left| \frac{\mathbf{r}_{Aj} \times (\mathbf{I}_B \times \mathbf{r}_{Bj})}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right| \right\rangle.$$

Recalling that $\mathbf{A} \times (\mathbf{B} \times \mathbf{C}) = \mathbf{B}(\mathbf{A} \cdot \mathbf{C}) - \mathbf{C}(\mathbf{A} \cdot \mathbf{B})$ this term (called the *diamagnetic spin–orbit contribution*, DSO^{77}) reads as

diamagnetic
spin–orbit

$$E_{\text{DSO}} = \frac{e^2}{2mc^2} \sum_{A,B} \sum_j \gamma_A \gamma_B \mathbf{I}_A \cdot \left[\mathbf{I}_B \left\langle \psi_0^{(0)} \left| \frac{\mathbf{r}_{Aj} \cdot \mathbf{r}_{Bj}}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right| \right\rangle - \left\langle \psi_0^{(0)} \left| \mathbf{r}_{Bj} \frac{\mathbf{r}_{Aj} \cdot \mathbf{I}_B}{r_{Aj}^3 r_{Bj}^3} \psi_0^{(0)} \right| \right] \right].$$

⁷⁷The name comes, of course, from the nuclear spin–electronic orbit interaction.

We see that we need to calculate some integrals with mono-electronic operators, which is an easy task.

12.11.2 PARAMAGNETIC CONTRIBUTIONS

The paramagnetic contribution E_{para} to the energy resulting from the perturbation given in eq. (12.68) can be written in a simpler form using the reduced resolvent \hat{R}_0 of eq. (10.62):

$$\begin{aligned} E_{\text{para}} &= \sum_k \frac{\langle \psi_0^{(0)} | (\hat{B}_3 + \hat{B}_6 + \hat{B}_7) \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | (\hat{B}_3 + \hat{B}_6 + \hat{B}_7) \psi_0^{(0)} \rangle}{E_0^{(0)} - E_k^{(0)}} \\ &= \langle \psi_0^{(0)} | (\hat{B}_3 + \hat{B}_6 + \hat{B}_7) \hat{R}_0 (\hat{B}_3 + \hat{B}_6 + \hat{B}_7) \psi_0^{(0)} \rangle \\ &= E_{\text{PSO}} + E_{\text{SD}} + E_{\text{FC}} + \text{mixed terms}, \end{aligned}$$

where

paramagnetic
spin-orbit

- the *paramagnetic spin-orbit contribution*:

$$E_{\text{PSO}} = \langle \psi_0^{(0)} | \hat{B}_3 \hat{R}_0 \hat{B}_3 \psi_0^{(0)} \rangle$$

with \hat{B}_3 meaning the interaction between the *nuclear spin* magnetic moment and the magnetic moment resulting from the *electronic angular momenta* of the individual electrons in an atom,

spin-dipole

- the *spin-dipole contribution*

$$E_{\text{SD}} = \langle \psi_0^{(0)} | \hat{B}_6 \hat{R}_0 \hat{B}_6 \psi_0^{(0)} \rangle,$$

which describes the interaction energy of the magnetic spin dipoles: the nuclear with the electronic dipole,

Fermi contact

- the *Fermi contact interaction*

$$E_{\text{FC}} = \langle \psi_0^{(0)} | \hat{B}_7 \hat{R}_0 \hat{B}_7 \psi_0^{(0)} \rangle,$$

which is related to the electronic spin-nuclear spin interaction with zero distance between them.

- the mixed terms contain $\langle \psi_0^{(0)} | \hat{B}_i \hat{R}_0 \hat{B}_j \psi_0^{(0)} \rangle$ for $i, j = 3, 6, 7$ and $i \neq j$. These terms are either exactly zero or (in most cases, not always) small.⁷⁸

⁷⁸Let us consider all cross terms. First, let us check that $\langle \psi_0^{(0)} | \hat{B}_3 \hat{R}_0 \hat{B}_6 \psi_0^{(0)} \rangle = \langle \psi_0^{(0)} | \hat{B}_6 \hat{R}_0 \hat{B}_3 \psi_0^{(0)} \rangle = \langle \psi_0^{(0)} | \hat{B}_3 \hat{R}_0 \hat{B}_7 \psi_0^{(0)} \rangle = \langle \psi_0^{(0)} | \hat{B}_7 \hat{R}_0 \hat{B}_3 \psi_0^{(0)} \rangle = 0$. Note, that \hat{B}_6 and \hat{B}_7 both contain electron spin operators, while \hat{B}_3 does not. Let us assume that, as it is usually the case, $\psi_0^{(0)}$ is a singlet function. Recalling eq. (10.62) this implies that for $\langle \psi_0^{(0)} | \hat{B}_3 \psi_k^{(0)} \rangle$ to survive, the function $\psi_k^{(0)}$ has to have the same multiplicity as $\psi_0^{(0)}$. This however kills the other factors: $\langle \psi_0^{(0)} | \hat{B}_6 \psi_k^{(0)} \rangle$ and $\langle \psi_0^{(0)} | \hat{B}_7 \psi_k^{(0)} \rangle$, terms describing the magnetic interaction of nuclei with exactly the same role played by electrons with α and β spins. Thus, the products $\langle \psi_0^{(0)} | \hat{B}_3 \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{B}_6 \psi_0^{(0)} \rangle$ and $\langle \psi_0^{(0)} | \hat{B}_3 \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{B}_7 \psi_0^{(0)} \rangle$ are zero.

12.11.3 COUPLING CONSTANTS

The energy contributions have to be averaged over rotations of the molecule and the coupling constants are to be extracted from the resulting formulae. How this is performed is shown in Appendix W on p. 1032.

Finally, the nuclear spin–spin coupling constant is calculated as the sum of the diamagnetic (J_{AB}^{DSO}) and paramagnetic contributions (J_{AB}^{PSO} , J_{AB}^{SD} , J_{AB}^{FC} , J_{AB}^{mixed})

$$J_{AB} = J_{AB}^{\text{dia}} + J_{AB}^{\text{para}}, \quad (12.94)$$

$$J_{AB}^{\text{dia}} \equiv J_{AB}^{\text{DSO}}, \quad (12.95)$$

$$J_{AB}^{\text{para}} = J_{AB}^{\text{PSO}} + J_{AB}^{\text{SD}} + J_{AB}^{\text{FC}} + J_{AB}^{\text{mixed}}, \quad (12.96)$$

where the particular contributions to the coupling constant are:⁷⁹

$$J_{AB}^{\text{DSO}} = \frac{e^2 \hbar}{3\pi m c^2} \gamma_A \gamma_B \sum_j \left\langle \psi_0^{(0)} \left| \frac{\mathbf{r}_{Aj} \cdot \mathbf{r}_{Bj}}{r_{Aj}^3 r_{Bj}^3} \right| \psi_0^{(0)} \right\rangle,$$

$$J_{AB}^{\text{PSO}} = \frac{1}{3\pi} \hbar \left(\frac{e}{mc} \right)^2 \gamma_A \gamma_B \sum_{j,l,Aj} \langle \psi_0^{(0)} | \hat{\mathbf{L}}_{Aj} \hat{R}_0 \hat{\mathbf{L}}_{Bl} \psi_0^{(0)} \rangle,$$

$$J_{AB}^{\text{SD}} = \frac{1}{3\pi} \hbar \gamma_{\text{el}}^2 \gamma_A \gamma_B \times \sum_{j,l=1}^N \left\langle \psi_0^{(0)} \left| \left[\frac{\hat{\mathbf{s}}_j}{r_{Aj}^3} - 3 \frac{(\hat{\mathbf{s}}_j \cdot \mathbf{r}_{Aj}) \mathbf{r}_{Aj}}{r_{Aj}^5} \right] \hat{R}_0 \left[\frac{\hat{\mathbf{s}}_l}{r_{Bl}^3} - 3 \frac{(\hat{\mathbf{s}}_l \cdot \mathbf{r}_{Bl}) \mathbf{r}_{Bl}}{r_{Bl}^5} \right] \right| \psi_0^{(0)} \right\rangle,$$

$$J_{AB}^{\text{FC}} = \frac{1}{3\pi} \hbar \left(\frac{8\pi}{3} \right)^2 \gamma_{\text{el}}^2 \gamma_A \gamma_B \sum_{j,l=1} \langle \psi_0^{(0)} | \delta(\mathbf{r}_{Aj}) \hat{\mathbf{s}}_j \hat{R}_0 \delta(\mathbf{r}_{Bl}) \hat{\mathbf{s}}_l \psi_0^{(0)} \rangle.$$

Thus, the nuclear spin magnetic moments are coupled *via* their magnetic interaction with the *electronic* magnetic moments:

- the $J_{AB}^{\text{DSO}} + J_{AB}^{\text{PSO}}$ results from the electronic *orbital* magnetic dipole moments,
- while $J_{AB}^{\text{SD}} + J_{AB}^{\text{FC}}$ corresponds to such interactions with the electronic *spin* magnetic dipole moments.

The mixed term $\langle \psi_0^{(0)} | \hat{B}_6 \hat{R}_0 \hat{B}_7 \psi_0^{(0)} \rangle$ vanishes for the isotropic electron cloud around the nucleus, because in the product $\langle \psi_0^{(0)} | \hat{B}_6 \psi_k^{(0)} \rangle \langle \psi_k^{(0)} | \hat{B}_7 \psi_0^{(0)} \rangle$ the Fermi term $\langle \psi_k^{(0)} | \hat{B}_7 \psi_0^{(0)} \rangle$ survives, if $\psi_0^{(0)} \psi_k^{(0)}$ calculated at the nucleus is non-zero. This kills, however, $\langle \psi_0^{(0)} | \hat{B}_6 \psi_k^{(0)} \rangle$, because for $\psi_0^{(0)} \psi_k^{(0)} \neq 0$ (which as a rule comes from a $1s$ orbital, this is isotropic situation) the electron–nucleus dipole–dipole magnetic interaction averages to zero when different positions of the electron are considered. For non-isotropic cases this mixed contribution can be of importance.

⁷⁹The empirical Hamiltonian (12.83) contains only the $A > B$ contributions, therefore the factor 2 appears in J .

As to the integrals involved, the Fermi contact contribution J_{AB}^{FC} (just the value of the wave function at the nucleus position) is the easiest to compute. Assuming that $\psi_k^{(0)}$ states are Slater determinants, the diamagnetic spin-orbit contribution J_{AB}^{DSO} requires some (easy) one-electron integrals of the type $\langle \psi_1 | \frac{x_{Aj}}{r_{Aj}^3} \psi_2 \rangle$, the paramagnetic spin-orbit contribution J_{AB}^{PSO} needs some one-electron integrals involving \hat{L}_{Aj} operators, which require differentiation of the orbitals, the spin-dipole contribution J_{AB}^{SD} leads also to some simple one-electron integrals, but handling the spin operators is needed (see p. 28), as for J_{AB}^{FC} . All the formulae require an infinite summation over states (due to the presence of \hat{R}_0), which is very tedious. This is why, in contemporary computational technique, some other approaches, mainly what is called propagator theory, are used.⁸⁰

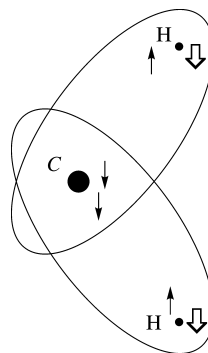
12.11.4 THE FERMİ CONTACT COUPLING MECHANISM

There are no simple rules, but usually the most important contribution to J_{AB} comes from the Fermi contact term (J_{AB}^{FC}), the next most important is paramagnetic spin-orbit term J_{AB}^{PSO} , other terms, including the mixed contributions J_{AB}^{mixed} , are of small importance. Let us consider the Fermi contact coupling mechanism between two protons through a single bond (the coupling constant J_{AB} denoted as $^1J_{HH}$). The proton and the electron close to it prefer to have opposite spins. Then the other electron of the bond (being closer to the other nucleus) shows the other nucleus the spin of first nucleus, therefore the second nucleus prefers to have the opposite spin with respect to the first nucleus. According to eq. (12.83), since $m_I, a m_{I,B} < 0$, this means $J_{AB} \equiv ^1J_{HH} > 0$. What about $^2J_{HH}$? This time, to have a through-bond interaction we have to have a central atom, like carbon ^{12}C (i.e. with zero magnetic moment), Fig. 12.15. The key point now is what happens at the central atom: whether it is preferable to have on it two parallel or two antiparallel electron spins? We do not know, but we may have a suggestion. Hund's rule says that, in case of orbital degeneracy (in our case: this corresponds to two *equivalent* C–H bonds), the electrons prefer to have parallel spins. This suggests that the two distant proton spins have a negative coupling constant, i.e. $^2J_{HH} < 0$, which is indeed the case. The same argument suggests that $^3J_{HH} > 0$, etc.⁸¹

⁸⁰J. Linderberg, Y. Öhrn, "Propagators in Quantum Chemistry", 2nd edition, John Wiley & Sons, Ltd, 2004.

⁸¹Thus, although calculation of the coupling constants is certainly complex, we have in mind a simple model of the nuclear spin-spin interaction that seems to work. We love such models, because they enable us to predict numbers knowing other numbers, or to predict new phenomena. This gives the impression that we understand what happens. This is by no means true. What the electrons are doing and how the spin magnetic moments interact is too complicated, but nevertheless we may suspect the main principles of the game. Such models help us to discuss things with others, to communicate some conjectures, to verify them, and to get more and more confidence in ourselves. Until one day something goes wrong. Then we try to understand why it happened. This *may* require a revision of our model, i.e. a new model, etc.

Fig. 12.15. Is the proton–proton coupling constant through two bonds (H–C–H), i.e. is $^2J_{HH}$ positive or negative? Please recall that $^1J_{HH} > 0$, see Fig. 12.13a, where the induction mechanism is described. The interaction of proton spins (wide arrows) through two bonds depends on what happens at the central carbon atom: are the spins of the two electrons there (one from each bond C–H) parallel or antiparallel? Hund’s rule suggests they prefer to be parallel. This means that the situation with the two proton spins parallel is more energetically favourable, and this means $^2J_{HH} < 0$. This rule of thumb may fail when the carbon atom participates in multiple bonds, as in ethylene, see section “From the research front”.



12.12 GAUGE INVARIANT ATOMIC ORBITALS (GIAO)

The coupling constants in practical applications may depend on the choice of vector and scalar potentials. The arbitrariness in the choice of the potentials A and ϕ (“gauge choice”) does not represent any problem for an *atom*, because it is natural to locate the origin (related to the formula (G.13) on p. 964) on the nucleus. The same reasoning however means a serious problem for a molecule, because even though any choice is equally justified, this justification is only theoretical, not practical. Should the origin be chosen at the centre of mass, at the centre of the electron cloud, halfway between them, or at another point? *An unfortunate (although mathematically fully justified) choice of the vector potential origin would lead to correct results, but only after calculating and summing up all the contributions to infinity, including application of the complete set of atomic orbitals.* These requirements are too demanding.

12.12.1 LONDON ORBITALS

Atomic orbitals are used in quantum chemistry as the building blocks of many-electron functions (cf. p. 357). Where to centre the orbitals sometimes represents a serious problem. On top of this, in the case of a magnetic field, there is, additionally, the above mentioned arbitrariness of choice of the vector potential origin. A remedy to the second problem was found by Fritz London⁸² in the form of atomic orbitals that depend explicitly on the field applied. Each atomic orbital $\chi(\mathbf{r} - \mathbf{R}_C)$ centred on nucleus C (with position shown by vector \mathbf{R}_C) and describing an electron pointed by vector \mathbf{r} , is replaced by the *London orbital* in the following way

London orbital

LONDON ATOMIC ORBITALS

$$\chi_L(\mathbf{r} - \mathbf{R}_C; A_C) = \exp(-iA_C \cdot \mathbf{r})\chi(\mathbf{r} - \mathbf{R}_C), \quad (12.97)$$

⁸²F. London, *J. Phys. Radium* 8 (1937) 397.

where A_C stands for the value of vector field A at nucleus C , and A corresponds to the origin O according to formula (G.13) on p. 964, where H denotes the intensity of a homogeneous magnetic field (no contribution from the magnetic field created by the nuclei, etc.).

As seen, the London orbitals are not invariant with respect to the choice of vector potential origin,

e.g., with respect to shifting the origin of the coordinate system in formula (G.13) by vector R :

$$A'(r) = \frac{1}{2}[H \times (r - R)] = A(r) - \frac{1}{2}[H \times R]. \quad (12.98)$$

Indeed,

$$\begin{aligned} \chi_L(r - R_C; A'_C) &= \exp(-iA'_C \cdot r) \chi(r - R_C) \\ &= \exp(-iA_C \cdot r) \exp\left(i\frac{1}{2}[H \times R] \cdot r\right) \chi(r - R_C) \\ &= \exp\left(i\frac{1}{2}[H \times R] \cdot r\right) \chi_L(r - R_C; A_C) \neq \chi_L(r - R_C; A_C). \end{aligned}$$

Despite this property the London orbitals are also known as Gauge Invariant Atomic Orbitals (GIAO).

12.12.2 INTEGRALS ARE INVARIANT

Let us calculate the overlap integral S between two London orbitals centred at points C and D . After shifting the origin of the coordinate system in eq. (G.13) by vector R we get

$$\begin{aligned} S &= \langle \chi_{L,1}(r - R_C; A'_C) | \chi_{L,2}(r - R_D; A'_D) \rangle \\ &= \langle \exp(-iA'_C \cdot r) \chi_1 | \exp(-iA'_D \cdot r) \chi_2 \rangle \\ &= \langle \chi_1 | \exp(-i(A'_D - A'_C) \cdot r) \chi_2 \rangle, \end{aligned}$$

i.e. *the result is independent of R* . It turns out⁸³ that all the integrals needed – those of kinetic energy, nuclear attraction and electron repulsion (cf. Appendix P on p. 1004) – are invariant with respect to an arbitrary shift of the origin of vector potential A .

This means that when we use the London orbitals the results do not depend on the choice of vector potential origin.

Summary

- The Hellmann–Feynman theorem tells us about the rate the energy changes, when we increase parameter P in the Hamiltonian (e.g., the intensity of the electric field). This

⁸³T. Helgaker, P. Jørgensen, *J. Chem. Phys.* 95 (1991) 2595.

rate is $\frac{\partial E}{\partial P} = \langle \psi(P) | \frac{\partial \hat{H}}{\partial P} | \psi(P) \rangle$, where $\psi(P)$ means the *exact* solution to the Schrödinger equation [with energy $E(P)$] at value P of the parameter.

ELECTRIC PHENOMENA

- When a molecule is located in an inhomogeneous electric field the perturbation operator has the form $\hat{H}^{(1)} = -\sum_q \hat{\mu}_q \mathcal{E}_q - \frac{1}{3} \sum_{qq'} \hat{\Theta}_{qq'} \mathcal{E}_{qq'} \dots$, where \mathcal{E}_q for $q = x, y, z$ denote the electric field components along the corresponding axes of a Cartesian coordinate system, $\mathcal{E}_{qq'}$ is the q' component of the gradient of \mathcal{E}_q , while $\hat{\mu}_q, \hat{\Theta}_{qq'}$ stand for the operators of the corresponding components of the dipole and quadrupole moments. In a homogeneous electric field ($\mathcal{E}_{qq'} = 0$) this reduces to $\hat{H}^{(1)} = -\sum_q \hat{\mu}_q \mathcal{E}_q$.
- After using the last expression in the Hellmann–Feynman theorem we obtain the dependence of the dipole moment components on the (weak) field intensity: $\mu_q = \mu_{0q} + \sum_{q'} \alpha_{qq'} \mathcal{E}_{q'} + \frac{1}{2} \sum_{qq'} \beta_{qq'q''} \mathcal{E}_q \mathcal{E}_{q'} \mathcal{E}_{q''} + \dots$, where μ_{0q} stands for the component corresponding to the isolated molecule, $\alpha_{qq'}$ denotes the q, q' component of the (dipole) polarizability tensor, $\beta_{qq'q''}$ is the corresponding component of the (dipole) first hyperpolarizability tensor, etc. The quantities $\mu_{0q}, \alpha_{qq'}, \beta_{qq'q''}$ in a given Cartesian coordinate system characterize the *isolated* molecule (no electric field) and represent the target of the calculation methods.
- Reversing the electric field direction may in general give different absolute values of the induced dipole moment only because of non-zero hyperpolarizability $\beta_{qq'q''}$ and higher-order hyperpolarizabilities.
- In an inhomogeneous field we have the following interactions:
 - of the *permanent dipole moment* of the molecule with the electric field $-\mu_0 \mathcal{E}$,
 - of the *induced dipole moment* proportional to the field ($\sum_{q'} \alpha_{qq'} \mathcal{E}_{q'}$) with the field plus higher-order terms proportional to higher powers of the field intensity involving *dipole hyperpolarizabilities*,
 - of the *permanent quadrupole moment* $\Theta_{qq'}$ of the molecule with the field gradient: $-\frac{1}{3} \sum_{qq'} \Theta_{qq'} \mathcal{E}_{qq'}$,
 - of the *induced quadrupole moment* proportional to the field gradient with the field gradient ($-\frac{1}{4} \sum_{qq'q''q'''} C_{qq'q''q'''} \mathcal{E}_{qq'} \mathcal{E}_{q''} \mathcal{E}_{q'''} \dots$, the quantity C is called the *quadrupole polarizability*) + higher-order terms containing *quadrupole hyperpolarizabilities*,
 - higher multipole interactions.
- In the LCAO MO approximation, the dipole moment of the molecule can be divided into the sum of the atomic dipole moments and the dipole moments of the atomic pairs.
- The dipole polarizability may be computed by:
 - the *Sum Over States method* (SOS), which is based on second-order correction to the energy in the perturbational approach;
 - the *finite field method*, e.g., a variational approach in which the interaction with a weak homogeneous electric field is included in the Hamiltonian. The components of the polarizability are computed as the second derivatives of the energy with respect to the corresponding field components (the derivatives are calculated at zero field). In practical calculations within the LCAO MO approximation we often use the Sadlej relation that connects the shift of a Gaussian atomic orbital with its exponent and the electric field intensity.
- In laser fields we may obtain a series of non-linear effects (proportional to higher powers of field intensity), including the doubling and tripling of the incident light frequency.

MAGNETIC PHENOMENA

- An elementary particle has a magnetic dipole moment \mathbf{M} proportional to its spin angular momentum \mathbf{I} , i.e. $\mathbf{M} = \gamma \mathbf{I}$, where γ stands for what is called the gyromagnetic factor (characteristic for the kind of particle).
- The magnetic dipole of a particle with spin \mathbf{I} (corresponding to spin quantum number I) in homogeneous magnetic field \mathbf{H} has $2I + 1$ energy states $E_{m_I} = -\gamma m_I \hbar H$, where $m_I = -I, -I + 1, \dots, +I$. Thus, the energy is proportional to H .
- The Hamiltonian of a system in an electromagnetic field has the form

$$\hat{H} = \sum_{j=1} \left[\frac{1}{2m_j} \left(\hat{\mathbf{p}}_j - \frac{q_j}{c} \mathbf{A}_j \right)^2 + q_j \phi_j \right] + \hat{V},$$

where \mathbf{A}_j and ϕ_j denote the vector and scalar fields at particle j (both are functions of position in the 3D space) that characterize the external electromagnetic field.

- \mathbf{A} and ϕ potentials contain, in principle (see Appendix G), the same information as the magnetic and electric field \mathbf{H} and \mathbf{E} . There is an arbitrariness in the choice of \mathbf{A} and ϕ .
- In order to calculate the energy states of a system of nuclei (detectable in NMR spectroscopy) we have to use the Hamiltonian \hat{H} given above, supplemented by the interaction of all magnetic moments related to the orbital and spin of the electrons and the nuclei.
- The refinement is based on classical electrodynamics and the usual quantum mechanical rules for forming operators (Chapter 1) or, alternatively, on the relativistic Breit Hamiltonian (p. 131). This is how we get the Hamiltonian (12.66) which contains the usual non-relativistic Hamiltonian (12.67) plus the perturbation (12.68) with a number of terms (p. 657).
- Experimentalists use an empirical Hamiltonian (eq. (12.82)), in which they have the interaction of the nuclear spin magnetic moments with the magnetic field (the Zeeman effect), the latter weakened by the shielding of the nuclei by the electrons plus the dot products of the nuclear magnetic moments weighted by the coupling constants. The experiment gives both the shielding (σ_A) and the coupling (J_{AB}) constants.
- Nuclear spin coupling takes place through the induction mechanism in the chemical bond (cf. Figs. 12.13, 12.15). Of key importance for this induction is high electron density at the position of the nuclei (the so called Fermi contact term, Fig. 12.13).
- The theory of shielding and coupling constants was given by Ramsey. According to the theory, each quantity consists of diamagnetic and paramagnetic contributions. The diamagnetic term is easy to calculate, the paramagnetic one is more demanding.
- Each of the contributions to the shielding constant individually depends on the choice of the origin of the vector potential \mathbf{A} , while their sum is invariant with respect to this choice.
- The London atomic orbitals $\chi_L = \exp(-i\mathbf{A}_C \cdot \mathbf{r})\chi(\mathbf{r} - \mathbf{R}_C)$ used in calculations for a molecule in a magnetic field depend explicitly on that field, through the value \mathbf{A}_C of the vector potential \mathbf{A} calculated at the centre \mathbf{R}_C of the usual atomic orbital $\chi(\mathbf{r} - \mathbf{R}_C)$.
- The most important feature of London orbitals is that all the integrals appearing in calculations are invariant with respect to the origin of the vector potential. This is why results obtained using London orbitals are also independent of that choice.

Main concepts, new terms

Hellmann–Feynman theorem (p. 618)	NMR (p. 658)
Cartesian multipole moments (p. 624)	NMR Hamiltonian (p. 658)
dipole, quadrupole, octupole moments (p. 624)	shielding constants (p. 659)
multipole polarizability (p. 628)	spin–spin intermediate coupling (p. 659)
multipole hyperpolarizability (p. 628)	local field (p. 659)
induced dipole moment (p. 628)	chemical shift (p. 664)
ZDO (p. 635)	Ramsey theory (p. 666)
sum over states method (p. 635)	diamagnetic effect (p. 668)
finite field method (p. 639)	paramagnetic effect (p. 668)
Sadlej relation (p. 640)	coupling constant (p. 668)
second/third harmonic generation (p. 646)	direct spin–spin interaction (p. 669)
nuclear magnetic dipole (p. 648)	diamagnetic spin–orbit contribution (p. 669)
spin magnetic moment (p. 648)	paramagnetic spin–orbit (p. 670)
gyromagnetic factor (p. 648)	spin–dipole contribution (p. 670)
Bohr magneton (p. 648)	Fermi contact contribution (p. 670)
nuclear magneton (p. 648)	coupling mechanism (p. 672)
Maxwell equations (p. 962)	London orbitals (p. 673)
	GIAO (p. 673)

From the research front

The electric dipole (hyper)polarizabilities are not easy to calculate, because:

- the sum over states method (SOS) converges slowly, i.e. a huge number of states have to be taken into account, including those belonging to a continuum;
- the finite field method requires a large quantity of atomic orbitals with small exponents (they describe the lion's share of the electron cloud deformation), although, being diffuse, they do not contribute much to the minimized energy (and lowering the energy is the only indicator that tells us whether a particular function is important or not).

More and more often in their experiments chemists investigate *large* molecules. Such large objects cannot be described by “global” polarizabilities and hyperpolarizabilities (except perhaps optical properties, where the wave length is often much larger than size of molecule). How such large molecules function (interacting with other molecules) depends first of all on their local properties. We have to replace such characteristics by new ones offering atomic resolution, similar to those proposed in the techniques of Stone or Sokalski (p. 1018), where individual atoms are characterized by their multipole moments, polarizabilities, etc.

Even a few years ago, the shielding and especially spin–spin coupling constants were very hard to calculate with reasonable accuracy. Nowadays these quantities are computed routinely using commercial software with atomic London orbitals (or other than GIAO basis sets).

The current possibilities of the theory in predicting the nuclear shielding constants and the nuclear spin–spin coupling constants are shown in Tables 12.1 and 12.2. Note that the accuracy of the theoretical results for shielding constants is nearly the same as that of experiment. As to the spin–spin coupling constants, the theoretical results are only slightly off experimental values.

Table 12.1. Comparison of theoretical and experimental shielding constants. The shielding constant σ_A (unitless quantity) is (as usual) expressed in ppm, i.e. the number given has to be multiplied by 10^{-6} to obtain σ_A of eq. (12.83). The Hartree–Fock, MP2, MP4 results are calculated in J. Gauss, *Chem. Phys. Letters* 229 (1994) 198; the CCSD(T) in J. Gauss, J.F. Stanton, *J. Chem. Phys.* 104 (1996) 2574, and the CASSCF in K. Ruud, T. Helgaker, R. Kobayashi, P. Jørgensen, K.L. Bak, H.J. Jensen, *J. Chem. Phys.* 100 (1994) 8178. For the Hartree–Fock method see Chapter 8, for the other methods mentioned here, see Chapter 10. The references to the corresponding experimental papers are given in T. Helgaker, M. Jaszuński, K. Ruud, *Chem. Rev.* 99 (1999) 293. The experimental error is estimated for σ_H in ammonia as ± 1.0 , for σ_O as ± 17.2 , for σ_H in water as ± 0.015 , for σ_F as ± 6 , for σ_H in hydrogen fluoride as ± 0.2

Method	CH ₄		NH ₃		H ₂ O		HF	
	σ_C	σ_H	σ_N	σ_H	σ_O	σ_H	σ_F	σ_H
Hartree–Fock	194.8	31.7	262.3	31.7	328.1	30.7	413.6	28.4
MP2	201.0	31.4	276.5	31.4	346.1	30.7	424.2	28.9
MP4	198.6	31.5	269.9	31.6	337.5	30.9	418.7	29.1
CCSD(T)	198.9	31.6	270.7	31.6	337.9	30.9	418.6	29.2
CASSCF	200.4	31.19	269.6	31.02	335.3	30.21	419.6	28.49
experiment	198.7	30.61	264.54	31.2	344.0	30.052	410	28.5

Table 12.2. Comparison of theoretical and experimental spin–spin coupling constants ${}^nJ_{AB}$ for ethylene (n denotes the number of separating bonds), in Hz. For the methods used see Chapter 10. All references to experimental and theoretical results are in T. Helgaker, M. Jaszuński, K. Ruud, *Chem. Rev.* 99 (1999) 293

Method	Spin–spin coupling constants J_{AB} for ethylene, in Hz					
	${}^1J_{CC}$	${}^1J_{CH}$	${}^2J_{CH}$	${}^2J_{HH}$	${}^3J_{HH-cis}$	${}^3J_{HH-trans}$
MC SCF	71.9	146.6	−3.0	−2.7	10.9	18.1
EOM-CCSD	70.1	153.23	−2.95	0.44	11.57	17.80
experiment	67.457	156.302	−2.403	2.394	11.657	19.015

Ad futurum...

It seems that the SOS method will be gradually sent out of business. The finite field method (in the electric field responses) will become more and more important, due to its simplicity. It remains however to solve the problem, how to process the information we get from such computations and translate it into the above mentioned local characteristics of the molecule.

Contemporary numerical methods allow routine calculation of polarizability. It is difficult with the hyperpolarizabilities that are much more sensitive to the quality of the atomic basis set used. The hyperpolarizabilities relate to non-linear properties, which are in high demand in new materials for technological applications.

Such problems as the dependence of the molecular spectra and of the molecular conformations and structure on the external electric field (created by our equipment or by a neighbouring molecule) will become more and more important.

The theory of the molecular response to an electric field and the theory of the molecular response to a magnetic field, despite some similarities, look as if they were “from another story”. One of the reasons is that the electric field response can be described by solving the Schrödinger equation, while that corresponding to the magnetic field is based inherently

on relativistic effects. The latter ones are much less investigated except some quite simple examples. Another reason may be the scale difference: the electric effects are much larger than the magnetic ones.

However, the theory for the interaction of matter with the electromagnetic field has to be coherent. The finite field method, so gloriously successful in electric field effects, is in the “stone age” stage for magnetic field effects. The propagator methods⁸⁴ look the most promising, these allow for easier calculation of NMR parameters than the sum-over-states methods.

Additional literature

A.D. Buckingham, *Advan. Chem. Phys.* 12 (1967) 107.

A classical paper on molecules in a static or periodic electric field.

H.F. Hameka, “Advanced Quantum Chemistry. Theory of Interactions between Molecules and Electromagnetic Fields”, Addison-Wesley Publishing Co., Reading, Massachusetts, USA (1965).

This is a first class book, although it presents the state of the art before the *ab initio* methods for calculating the magnetic properties of molecules.

T. Helgaker, M. Jaszuński, K. Ruud, *Chem. Rev.* 99 (1999) 293.

A competent review article on the magnetic properties of molecules (NMR) with presentation of suitable contemporary theoretical methods.

Questions

- The Hellmann–Feynman theorem says that (\hat{H} means the Hamiltonian depending on the parameter P):
 - $\frac{\partial E}{\partial P} = \langle \psi | \frac{\partial \hat{H}}{\partial P} | \psi \rangle$, if ψ is the variational trial function;
 - $\frac{\partial E}{\partial P} = \langle \psi | \frac{\partial \hat{H}}{\partial P} | \psi \rangle$, if ψ is the Hartree–Fock wave function;
 - $\frac{\partial E}{\partial P} = \langle \psi | \frac{\partial \hat{H}}{\partial P} | \psi \rangle$, for any normalized ψ ;
 - $\frac{\partial E}{\partial P} = \langle \psi | \frac{\partial \hat{H}}{\partial P} | \psi \rangle$, if ψ is an eigenfunction of \hat{H} .
- The proportionality constant at the third-power term (the powers of electric field intensity) in the expression for the energy of a molecule in a homogeneous electric field is:
 - a component of the quadrupole moment;
 - a component of the dipole moment;
 - $-\frac{1}{3!}\beta$, where β denotes a hyperpolarizability component;
 - a component of the octupole moment.
- A non-polar molecule (with a non-zero quadrupolar moment) in an electric field with a non-zero gradient:
 - does not interact with the field;
 - will rotate to align its dipole moment along the field;
 - will orient to align its longer quadrupole axis along the field;
 - will orient to align its longer quadrupole axis along the gradient of the field.

⁸⁴J. Linderberg, Y. Öhrn, “*Propagators in Quantum Chemistry*”, 2nd edition, John Wiley & Sons, Ltd, 2004.

4. Second harmonic generation requires that the molecule has:
 - a) large dipole hyperpolarizabilities;
 - b) large quadrupole and octupole polarizabilities;
 - c) large octupole and higher order hyperpolarizabilities;
 - d) a large quadrupole hyperpolarizability.
5. In variational calculations for the benzene molecule (zero electric field) the GTO exponents and positions have been optimized. A small shift of the GTOs when using a finite field method:
 - a) will always lower the energy;
 - b) always increases the energy;
 - c) will increase the energy if the GTOs move in the direction of the field and decrease if they move in the opposite direction;
 - d) will always give a polarizability greater than zero.
6. The magnetic moment \mathbf{M} of a particle:
 - a) always has the direction of the particle's spin angular momentum;
 - b) its length is always an integer or half-integer;
 - c) interacts with a homogeneous magnetic field \mathbf{H} , and the interaction energy is equal to $\frac{1}{2}\mathbf{M}\mathbf{H}^2$;
 - d) interacts with a homogeneous magnetic field \mathbf{H} , and the interaction energy is equal to $-\mathbf{H} \cdot \mathbf{M}$.
7. If we choose the vector potential $\mathbf{A}(\mathbf{r}) = \frac{1}{2}[\mathbf{H} \times \mathbf{r}]$, where \mathbf{H} is the magnetic field intensity, then:
 - a) we have $\nabla \mathbf{A} = 0$ and \mathbf{A} agrees with the Maxwell equations;
 - b) $\mathbf{A}(\mathbf{r})$ is a homogeneous field;
 - c) $\mathbf{A}(\mathbf{r})$ is directed towards the origin;
 - d) $\mathbf{A}(\mathbf{r})$ is parallel to \mathbf{H} .
8. The vector potential $\mathbf{A}(\mathbf{r})$ of electromagnetic field corresponds to homogeneous magnetic field \mathbf{H} . Then \mathbf{A} :
 - a) is uniquely determined from the Maxwell equation;
 - b) is uniquely determined from the Maxwell equation $\mathbf{A} = \text{curl } \mathbf{H}$;
 - c) is also a homogeneous field;
 - d) $\text{curl}[\mathbf{A} - \nabla(x^2 + y^2 + z^2)] = \mathbf{H}$.
9. A nuclear shielding constant consists of diamagnetic and paramagnetic parts. Each of these parts:
 - a) represents a second-order effect in perturbation theory;
 - b) represents a first-order effect in perturbation theory;
 - c) changes when the origin of the vector potential \mathbf{A} changes;
 - d) represents the Fermi contact term.
10. The London or Gauge-Invariant Atomic Orbital $\chi_L(\mathbf{r} - \mathbf{R})$:
 - a) depends on the vector potential calculated at position \mathbf{R} ;
 - b) depends on the vector potential calculated at position \mathbf{r} ;
 - c) does not depend on the vector potential;
 - d) depends on the vector potential at the point shown by $\mathbf{r} - \mathbf{R}$.

Answers

1d, 2c, 3d, 4a, 5c, 6d, 7a, 8d, 9c, 10a