Chapter 15
Coupling to Electromagnetic Fields

Electromagnetism is the most important interaction for the study of atoms, molecules and materials. It determines most of the potentials or perturbation operators V which are studied in practical applications of quantum mechanics, and it also serves as a basic example for the implementation of other, more complicated interactions in quantum mechanics. Therefore the primary objective of the current chapter is to understand how electromagnetic fields are introduced in the Schrödinger equation.

15.1 Electromagnetic couplings

The introduction of electromagnetic fields into the Schrödinger equation for a particle of mass m and electric charge q can be inferred from the description of the particle in classical Lagrangian mechanics.

The Lagrange function for the particle in electromagnetic fields

$$\boldsymbol{E}(\boldsymbol{x},t) = -\nabla\Phi(\boldsymbol{x},t) - \frac{\partial\boldsymbol{A}(\boldsymbol{x},t)}{\partial t}, \quad \boldsymbol{B}(\boldsymbol{x},t) = \nabla\times\boldsymbol{A}(\boldsymbol{x},t)$$

is

$$L = \frac{m}{2}\dot{\boldsymbol{x}}(t)^2 + q\dot{\boldsymbol{x}}(t)\cdot\boldsymbol{A}(\boldsymbol{x}(t),t) - q\Phi(\boldsymbol{x}(t),t). \tag{15.1}$$

Let us check (or review) that equation (15.1) is indeed the correct Lagrange function for the particle. The electromagnetic potentials in the Lagrange function depend on the time t both explicitly and implicitly through the time dependence $\boldsymbol{x}(t)$ of the trajectory of the particle. The time derivative of the conjugate momentum

$$\boldsymbol{p} = \frac{\partial L}{\partial\dot{\boldsymbol{x}}} = m\dot{\boldsymbol{x}} + q\boldsymbol{A} \tag{15.2}$$

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is therefore

$$\frac{d\boldsymbol{p}}{dt} = m\ddot{\boldsymbol{x}} + q\dot{x}_i\frac{\partial \boldsymbol{A}}{\partial x_i} + q\frac{\partial \boldsymbol{A}}{\partial t}.$$

According to the Euler-Lagrange equations (cf. Appendix A), this must equal

$$\frac{\partial L}{\partial \boldsymbol{x}} = q\dot{x}_i\nabla A_i - q\nabla\Phi.$$

The property (7.14) of the ϵ tensor implies

$$\boldsymbol{e}_i\left(\dot{x}_j\partial_i A_j - \dot{x}_j\partial_j A_i\right) = \boldsymbol{e}_i\epsilon_{ijk}\epsilon_{klm}\dot{x}_j\partial_l A_m = \dot{\boldsymbol{x}}\times\boldsymbol{B},$$

and therefore the Euler-Lagrange equation yields the Lorentz force law

$$m\ddot{\boldsymbol{x}} = q(\boldsymbol{E} + \boldsymbol{v}\times\boldsymbol{B})\,, \tag{15.3}$$

as required.

The classical Hamiltonian for the particle follows as

$$H = \boldsymbol{p}\cdot\dot{\boldsymbol{x}} - L = \frac{1}{2m}(\boldsymbol{p} - q\boldsymbol{A})^2 + q\Phi = \frac{m}{2}\dot{\boldsymbol{x}}^2 + q\Phi. \tag{15.4}$$

The Hamilton operator of the charged particle therefore becomes

$$H = \frac{1}{2m}[\mathbf{p} - q\boldsymbol{A}(\mathbf{x},t)]^2 + q\Phi(\mathbf{x},t), \tag{15.5}$$

and the Schrödinger equation in $\boldsymbol{x}$ representation is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi(\boldsymbol{x},t) = -\frac{1}{2m}[\hbar\nabla - \mathrm{i}q\boldsymbol{A}(\boldsymbol{x},t)]^2\Psi(\boldsymbol{x},t) + q\Phi(\boldsymbol{x},t)\Psi(\boldsymbol{x},t). \tag{15.6}$$

This is the Schrödinger equation for a charged particle in electromagnetic fields. If we write this in the form

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi - q\Phi\Psi = \frac{1}{2m}(\mathrm{i}\hbar\nabla + q\boldsymbol{A})^2\Psi$$

we also recognize that this arises from the free Schrödinger equation through the substitutions

$$\mathrm{i}\hbar\nabla \to \mathrm{i}\hbar\nabla + q\boldsymbol{A}, \quad \mathrm{i}\hbar\frac{\partial}{\partial t} = \mathrm{i}\hbar c\partial_0 \to \mathrm{i}\hbar c\partial_0 - q\Phi. \tag{15.7}$$

These equations can be combined in 4-vector notation with $p_0 = -E/c$, $A_0 = -\Phi/c$,

$$p_\mu = -\mathrm{i}\hbar\partial_\mu \to p_\mu - qA_\mu = -\mathrm{i}\hbar\partial_\mu - qA_\mu.$$

This observation is useful for recognizing a peculiar symmetry property of equation (15.6). Classical electromagnetism is invariant under gauge transformations of the electromagnetic potentials (here we use $f(x) \equiv f(\boldsymbol{x}, t)$),

$$\Phi(x) \to \Phi'(x) = \Phi(x) - c\partial_0\varphi(x), \quad \boldsymbol{A}(x) \to \boldsymbol{A}'(x) = \boldsymbol{A}(x) + \nabla\varphi(x), \tag{15.8}$$

where the arbitrary function $\varphi(x)$ has the dimension of a magnetic flux, i.e. it comes in units of Vs. The Schrödinger equation (15.6) should respect this invariance of classical electromagnetism to comply with classical limits, and indeed it does. If we also transform the wave function according to

$$\Psi(x) \to \Psi'(x) = \exp\!\left(\mathrm{i}\frac{q}{\hbar}\varphi(x)\right)\Psi(x), \tag{15.9}$$

then the Schrödinger equation in the transformed fields and wave functions has exactly the same form as the Schrödinger equation in the original fields, because the linear transformation property

$$\begin{aligned}
&\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi' - q\Phi'\Psi' + \frac{1}{2m}(\hbar\nabla - \mathrm{i}q\boldsymbol{A}')^2\Psi' \\
&= \exp\!\left(\mathrm{i}\frac{q}{\hbar}\varphi(x)\right)\left[\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi - q\Phi\Psi + \frac{1}{2m}(\hbar\nabla - \mathrm{i}q\boldsymbol{A})^2\Psi\right]
\end{aligned}$$

implies that

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi' - q\Phi'\Psi' + \frac{1}{2m}(\hbar\nabla - \mathrm{i}q\boldsymbol{A}')^2\Psi' = 0$$

holds in the transformed fields if and only if the Schrödinger equation also holds in the original fields,

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi - q\Phi\Psi + \frac{1}{2m}(\hbar\nabla - \mathrm{i}q\boldsymbol{A})^2\Psi = 0.$$

The reason for the linear transformation law is

$$\begin{aligned}
\partial_\mu - \mathrm{i}\frac{q}{\hbar}A'_\mu &= \partial_\mu - \mathrm{i}\frac{q}{\hbar}A_\mu - \mathrm{i}\frac{q}{\hbar}(\partial_\mu\varphi) \\
&= \exp\!\left(\mathrm{i}\frac{q}{\hbar}\varphi\right)\left(\partial_\mu - \mathrm{i}\frac{q}{\hbar}A_\mu\right)\exp\!\left(-\mathrm{i}\frac{q}{\hbar}\varphi\right),
\end{aligned}$$

which implies that the *covariant derivatives*

$$D_\mu \Psi = \left(\partial_\mu - \mathrm{i}\frac{q}{\hbar}A_\mu\right)\Psi$$

transform exactly like the fields,

$$\begin{aligned}
&\Psi(x) \to \Psi'(x) = \exp\!\left(\mathrm{i}\frac{q}{\hbar}\varphi(x)\right)\Psi(x),\\
&D_\mu\Psi(x) \to D'_\mu\Psi'(x) = \exp\!\left(\mathrm{i}\frac{q}{\hbar}\varphi(x)\right)D_\mu\Psi(x),\\
&D_\mu D_\nu \ldots D_\rho\Psi(x) \to D'_\mu D'_\nu \ldots D'_\rho\Psi'(x) = \exp\!\left(\mathrm{i}\frac{q}{\hbar}\varphi(x)\right)D_\mu D_\nu \ldots D_\rho\Psi(x).
\end{aligned}$$

This implies preservation of every partial differential equation which like the Schrödinger equation uses only covariant derivatives,

$$\mathrm{i}\hbar c D_0\Psi(x) = -\frac{\hbar^2}{2m}\boldsymbol{D}^2\Psi(x) \quad \Leftrightarrow \quad \mathrm{i}\hbar c D'_0\Psi'(x) = -\frac{\hbar^2}{2m}\boldsymbol{D}'^2\Psi'(x).$$

Coupling of matter wave functions to electromagnetic potentials through covariant derivatives is known as *minimal coupling*.

Observables are gauge invariant, too. For example, the mechanical momentum of the charged particle in electromagnetic fields is

$$\begin{aligned}
m\frac{d}{dt}\langle\boldsymbol{x}\rangle(t) &= \int d^3\boldsymbol{x}\,\Psi^+(\boldsymbol{x},t)\,[-\mathrm{i}\hbar\nabla - q\boldsymbol{A}(\boldsymbol{x},t)]\,\Psi(\boldsymbol{x},t)\\
&= \int d^3\boldsymbol{x}\,\Psi'^+(\boldsymbol{x},t)\left[-\mathrm{i}\hbar\nabla - q\boldsymbol{A}'(\boldsymbol{x},t)\right]\Psi'(\boldsymbol{x},t). \qquad (15.10)
\end{aligned}$$

Electromagnetic interactions ensure local phase invariance of nature. We can rotate the wave function with an arbitrary local phase factor without changing the dynamics or observables of a physical system, due to the presence of the electromagnetic potentials. In hindsight, we should consider this as the reason for the peculiar coupling of the electromagnetic potentials in the Schrödinger equation (15.6).

The presence of the electromagnetic potentials in the observables will of course affect conservation laws. E.g. the mechanical momentum (15.10) of the particle will generically not be conserved, because it can exchange momentum with the electromagnetic field which carries momentum $\boldsymbol{p}_{em}(t) = \epsilon_0\int d^3\boldsymbol{x}\,\boldsymbol{E}(\boldsymbol{x},t)\times\boldsymbol{B}(\boldsymbol{x},t)$. The conserved momentum[1] of the coupled system of non-relativistic charged

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[1] The canonical momentum $\langle\boldsymbol{p}\rangle(t) = -\mathrm{i}\hbar\int d^3\boldsymbol{x}\,\Psi^+(\boldsymbol{x},t)\boldsymbol{\nabla}\Psi(\boldsymbol{x},t) = m(d\langle\boldsymbol{x}\rangle(t)/dt) + q\langle\boldsymbol{A}(\boldsymbol{x},t)\rangle$ is also generically not conserved, except if the particle moves in a spatially homogeneous electric field $\boldsymbol{E}(t) = -d\boldsymbol{A}(t)/dt$, e.g. in a plate capacitor. However, note that this is an artifact of the gauge $\Phi = 0$.

particle and electromagnetic fields is

$$\boldsymbol{P} = m\frac{d}{dt}\langle\boldsymbol{x}\rangle(t) + \boldsymbol{p}_{em}(t) = \int d^3\boldsymbol{x}\,\mathcal{P}(\boldsymbol{x},t),$$

where the momentum density with symmetrized action of the derivatives on the wave functions is given by

$$\begin{aligned}\mathcal{P}(\boldsymbol{x},t) &= \frac{\hbar}{2\mathrm{i}}\left[\Psi^+(\boldsymbol{x},t)\cdot\nabla\Psi(\boldsymbol{x},t) - \nabla\Psi^+(\boldsymbol{x},t)\cdot\Psi(\boldsymbol{x},t)\right]\\ &\quad - q\Psi^+(\boldsymbol{x},t)\boldsymbol{A}(\boldsymbol{x},t)\Psi(\boldsymbol{x},t) + \epsilon_0\boldsymbol{E}(\boldsymbol{x},t)\times\boldsymbol{B}(\boldsymbol{x},t).\end{aligned} \tag{15.11}$$

The derivation of momentum conservation for the classical particle-field system in the full relativistic setting can be found in Appendix B, see in particular equation (B.29). Systematic derivations of momentum densities in the coupled system of charged particles and electromagnetic fields in the framework of relativistic spinor quantum electrodynamics (QED) can be found in Sections 21.4 and 21.5, see in particular equations (21.90) and (21.106). Problem 21.5 and equation (21.133) provide the corresponding results in relativistic scalar QED.

Both the non-relativistic limits for bosons and fermions lead to (15.11) for the conserved momentum density in non-relativistic QED, which is also known as *quantum electronics*.

Multipole moments

In many applications of quantum mechanics, simplifications of the electromagnetic coupling terms in equation (15.6) can be employed if the electromagnetic fields have large wavelengths compared to the wave functions in the Schrödinger equation. The leading order and most common approximation is related to the electric dipole moment of charge distributions, and therefore we will briefly discuss the origin of multipole moments in electromagnetism.

Suppose that we probe the electromagnetic potential of a charge q which is located at $\boldsymbol{x}$. We are interested in the potential at location $\boldsymbol{r}$, where $|\boldsymbol{r}| \gg |\boldsymbol{x}|$. Second order Taylor expansion of the Coulomb term in the variables $\boldsymbol{x}$ yields

$$\frac{q}{|\boldsymbol{r}-\boldsymbol{x}|} \approx \frac{q}{r} + q\frac{\boldsymbol{r}\cdot\boldsymbol{x}}{r^3} + q\frac{3(\boldsymbol{r}\cdot\boldsymbol{x})^2 - r^2\boldsymbol{x}^2}{2r^5} = \frac{q}{r} + \frac{\boldsymbol{r}\cdot\boldsymbol{d}}{r^3} + \frac{1}{2r^5}\boldsymbol{r}\cdot\underline{\mathrm{Q}}\cdot\boldsymbol{r}$$

with the dipole and quadrupole terms

$$\boldsymbol{d} = q\boldsymbol{x}, \quad \underline{\mathrm{Q}} = q\left(3\boldsymbol{x}\otimes\boldsymbol{x} - \boldsymbol{x}^2\underline{1}\right).$$

For an extended charge distribution $\varrho(\boldsymbol{x})$ this implies at large distance a representation of the potential

$$4\pi\epsilon_0\Phi(\boldsymbol{r}) = \int d^3\boldsymbol{x}\,\frac{\varrho(\boldsymbol{x})}{|\boldsymbol{r}-\boldsymbol{x}|} \approx \frac{q}{r} + \frac{\boldsymbol{r}\cdot\boldsymbol{d}}{r^3} + \frac{1}{2r^5}\boldsymbol{r}\cdot\underline{\mathrm{Q}}\cdot\boldsymbol{r}$$

in terms of the monopole, dipole, and quadrupole moments

$$q = \int d^3\boldsymbol{x}\,\varrho(\boldsymbol{x}), \quad \boldsymbol{d} = \int d^3\boldsymbol{x}\,\varrho(\boldsymbol{x})\boldsymbol{x}, \quad \underline{\mathrm{Q}} = \int d^3\boldsymbol{x}\,\varrho(\boldsymbol{x})[3\boldsymbol{x}\otimes\boldsymbol{x} - \boldsymbol{x}^2\underline{1}].$$

We will find that the leading order coupling of long wavelength electromagnetic fields to charges appears through electric dipole moments of the charges.

Semiclassical treatment of the matter-radiation system in the dipole approximation

In the semiclassical treatment the electromagnetic fields are considered as external classical fields with which the quantum mechanical matter (atom, nucleus, molecule, solid) interacts.

If we consider e.g. an atom with an internal (average or effective) potential $V_{int}(\boldsymbol{x})$ experienced by the electrons, the Schrödinger equation for these electrons in the external electromagnetic fields is

$$\mathrm{i}\hbar\frac{\partial}{\partial t}\Psi = -\frac{1}{2m}(\hbar\nabla - \mathrm{i}q\boldsymbol{A})^2\Psi + (q\Phi + V_{int})\Psi. \tag{15.12}$$

If the electromagnetic fields vary weakly over the extension a of the wave functions (corresponding to approximately homogeneous field over the extension of the atom or molecule under consideration), we can effectively assume a spatially homogeneous field $\boldsymbol{E} = \boldsymbol{E}(t)$ corresponding to a potential $\Phi(\boldsymbol{x},t) = -\boldsymbol{E}(t)\cdot\boldsymbol{x}$. If we assume that our material probes range over length scales from 1 Å (corresponding to the size of atoms) to several Å (corresponding to molecules containing e.g. several Benzene rings), electromagnetic fields with wavelengths larger than 100 nm or photon energies smaller than 12 eV can be considered as approximately spatially homogeneous over the size of the probe. Furthermore the magnetic field in the electromagnetic wave satisfies

$$\boldsymbol{B}(t) = \frac{1}{2}\nabla\times(\boldsymbol{B}(t)\times\boldsymbol{x}) \tag{15.13}$$

and

$$|\boldsymbol{B}| = \frac{1}{c}|\boldsymbol{E}|, \quad |\dot{\boldsymbol{B}}| = \frac{\omega}{c}|\boldsymbol{E}| = \frac{2\pi}{\lambda}|\boldsymbol{E}|.$$

We have

$$\left|\frac{\partial \boldsymbol{A}}{\partial t}\right| = \frac{1}{2}\left|\dot{\boldsymbol{B}} \times \boldsymbol{x}\right| \simeq \frac{\pi a}{\lambda}\,|\boldsymbol{E}| \ll |\boldsymbol{E}|\,,$$

and therefore the description of $\boldsymbol{E}$ only through the electric potential,

$$\boldsymbol{E}(t) = -\nabla\Phi(\boldsymbol{x},t) = \nabla(\boldsymbol{E}(t)\cdot\boldsymbol{x}),$$

is justified for $\lambda \gg a$. Furthermore, the magnitudes of magnetic contributions to the Schrödinger equation are of order

$$\frac{q\hbar}{m}\,|\boldsymbol{A}\cdot\nabla\Psi| \simeq \frac{q\hbar}{2mc}\,|\boldsymbol{E}|\,|\boldsymbol{x}|\,|\nabla\Psi| \simeq \frac{q\hbar}{2mc}\,|\boldsymbol{E}|\,|\Psi|\,, \tag{15.14}$$

$$\frac{q^2}{2m}\boldsymbol{A}^2\,|\Psi| \simeq \frac{q^2}{8mc^2}\boldsymbol{E}^2\boldsymbol{x}^2\,|\Psi| \simeq \frac{q^2a^2}{8mc^2}\boldsymbol{E}^2\,|\Psi|\,. \tag{15.15}$$

For comparison, the electric contribution has a magnitude of order

$$q\,|\boldsymbol{E}|\,|\boldsymbol{x}|\,|\Psi| \simeq qa\,|\boldsymbol{E}|\,|\Psi|\,.$$

The ratio of the linear magnetic term (15.14) to the electric term is $\hbar/(2mca)$. If we use the electron mass for m, we find

$$\frac{\hbar}{2mca} \leq 2\times 10^{-3}\times\frac{1\,\text{Å}}{a},$$

i.e. the linear magnetic term is often negligible compared to the electric term.

The ratio of the second magnetic term (15.15) to the electric term is approximately $qa\,|\boldsymbol{E}|\,/8mc^2$. Validity of the non-relativistic approximation requires that the electrostatic energy $qa\,|\boldsymbol{E}|$ due to the electric field should be small compared to mc^2. Therefore we also find that the second magnetic term should be negligible compared to the electric term. Quantitatively, if we assume $mc^2 = 511\,\text{keV}$, we have $ea\,|\boldsymbol{E}|\,/8mc^2 \ll 1$ for

$$|\boldsymbol{E}| \ll \frac{8mc^2}{ea} = 4\times 10^{16}\frac{\text{V}}{\text{m}}\times\frac{1\,\text{Å}}{a}.$$

For comparison, the internal field strength in hydrogen is of order $e/(4\pi\epsilon_0 a_0^2) \simeq 5\times 10^{11}\,\text{V/m}$.

We conclude that for $\lambda \gg a$ the effect of external electromagnetic fields can be approximated by the addition of a term

$$\Delta V(\mathbf{x},t) = q\Phi(\mathbf{x},t) = -\,q\boldsymbol{E}(t)\cdot\mathbf{x} = -\,\boldsymbol{d}\cdot\boldsymbol{E}(t) \tag{15.16}$$

in the Schrödinger equation. The approximation of spatially homogeneous external field yields a perturbation proportional to the dipole operator and is therefore denoted as *dipole approximation*.

Two cautionary remarks are in order at this point. The term *dipole approximation* is nowadays more widely used for the long wavelength approximation $\exp(\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}) \simeq 1$ in matrix elements irrespective of whether the perturbation operator has the dipole form (15.16) or is given in terms of the coupling to the vector potential $\boldsymbol{A}(\mathbf{x},t)$ in (15.12).

Furthermore, if we describe electromagnetic interactions at the level of photon-matter interactions, the dipole approximation (15.16) is generically limited to first order perturbation theory, and holds in second order perturbation theory only if additional conditions are met, see Section 18.9 and Problem 18.10.

Dipole selection rules

The first order scattering matrix elements in dipole approximation are given by $S_{fi} = \sqrt{2\pi}\mathrm{i}q\boldsymbol{E}(\omega_{fi})\cdot\langle f|\mathbf{x}|i\rangle/\hbar$, i.e. only transitions $|i\rangle \to |f\rangle$ with non-vanishing dipole matrix elements $q\langle f|\mathbf{x}|i\rangle$ are allowed in this approximation. This yields straightforward selection rules for states which are eigenstates of $\boldsymbol{M}^2$ and M_z. The commutator relation $[M_z, \mathrm{z}] = 0$ implies

$$\langle n', \ell', m'|[M_z, \mathrm{z}]|n, \ell, m\rangle = \hbar\langle n', \ell', m'|\mathrm{z}|n, \ell, m\rangle(m' - m) = 0, \tag{15.17}$$

and therefore an electric field component in z direction can only induce transitions between states with the same magnetic quantum number.

In the same way, the commutators $[M_z, \mathrm{x} \pm \mathrm{iy}] = \pm\hbar(\mathrm{x} \pm \mathrm{iy})$ imply

$$\langle n', \ell', m'|\mathrm{x} \pm \mathrm{iy}|n, \ell, m\rangle(m' - m \mp 1) = 0, \tag{15.18}$$

such that electric field components in the (x, y) plane can only induce transitions which increase or decrease the magnetic quantum number by one unit.

Finally, the fairly complicated relation $[\boldsymbol{M}^2, [\boldsymbol{M}^2, \mathbf{x}]] = 2\hbar^2\{\boldsymbol{M}^2, \mathbf{x}\}$ yields

$$\langle n', \ell', m'|\mathbf{x}|n, \ell, m\rangle(\ell + \ell')(\ell + \ell' + 2)[(\ell - \ell')^2 - 1] = 0. \tag{15.19}$$

This implies that the matrix element can be non-vanishing only if $\ell' = \ell \pm 1$. $\ell' = \ell = 0$ is not a solution, because in this case the wave functions depend only on r and the angular integrations then show that the matrix element vanishes.

Equations (15.17–15.19) imply the dipole selection rules $\Delta\ell = \pm 1$ and $\Delta m = 0, \pm 1$.

15.2 Stark effect and static polarizability tensors

Polarizability tensors characterize the response of a quantum system to an external electric field $\boldsymbol{E}$. The calculation of polarizability tensors is another example of applications of second order perturbation theory in materials science. It also illustrates the role of perturbation theory in derivations of quantum mechanical expressions for measurable physical quantities, which were first introduced in classical electrodynamics and were initially approximated by means of simple mechanical models.

The calculation of polarizabilities generically involves many particles and related dipole operators $V(t) = -\sum_{i=1}^{N} q_i\boldsymbol{E}(t)\cdot\mathbf{x}_i$, where it is assumed that all particles are confined to a region which is still small compared to the wavelength of the electric field. We will develop the theory in a single-particle approximation in the sense that we only use the single charged (quasi)particle operator $V(t) = -q\boldsymbol{E}(t)\cdot\mathbf{x}$. In the present section we will do this for time-independent external field, where we can use the techniques of time-independent perturbation theory. The case of dynamical polarizability for time-dependent external fields will be discussed in Section 15.3.

Linear Stark effect

Before we jump into the second order calculation of the response to an electric field, we consider the implications of first order perturbation theory for the dipole approximation.

An external static electric field shifts the Hamilton operator according to

$$H_0 \to H = H_0 + V = H_0 - q\boldsymbol{E}\cdot\mathbf{x}.$$

Time-independent perturbation theory tells us that the first order shifts of atomic or molecular energy levels due to the external field have to be determined as the eigenvalues of the matrix

$$\langle\Psi_{n,\alpha}^{(0)}|V(\mathbf{x})|\Psi_{n,\beta}^{(0)}\rangle = -q\langle\Psi_{n,\alpha}^{(0)}|\mathbf{x}|\Psi_{n,\beta}^{(0)}\rangle\cdot\boldsymbol{E},$$

and when the n-th degeneracy subspace has been internally diagonalized with respect to $V(\mathbf{x})$, the first order shifts are

$$E_{n,\alpha}^{(1)} = -q\langle\Psi_{n,\alpha}^{(0)}|\mathbf{x}|\Psi_{n,\alpha}^{(0)}\rangle\cdot\boldsymbol{E} = -\boldsymbol{d}_{n,\alpha}\cdot\boldsymbol{E},$$

with the *intrinsic* dipole moment in the state $|\Psi_{n,\alpha}^{(0)}\rangle$

$$\boldsymbol{d}_{n,\alpha} = q\langle\Psi_{n,\alpha}^{(0)}|\mathbf{x}|\Psi_{n,\alpha}^{(0)}\rangle. \tag{15.20}$$

The perturbation V has odd parity under $\boldsymbol{x} \to -\boldsymbol{x}$, while atomic states of opposite parity are usually not degenerate. Therefore in systems which are symmetric under the parity transformation $\boldsymbol{x} \to -\boldsymbol{x}$, the states in the n-th energy level usually satisfy

$$\langle \Psi^{(0)}_{n,\alpha} | \mathbf{x} | \Psi^{(0)}_{n,\beta} \rangle = 0$$

because the integrand is odd under the parity transformation. Usually this implies absence of a linear Stark effect in atoms, and the same remark applies to molecules with parity symmetry. An important exception is the hydrogen atom due to ℓ-degeneracy of its energy levels (if the matrix elements of V are larger than the fine structure of the hydrogen levels). States with angular momentum quantum number ℓ have parity $(-1)^{\ell}$, so that the n-th hydrogen level with $n > 1$ contains degenerate states of opposite parity. Diagonalization of V in that degeneracy subspace then yields states $|\Psi^{(0)}_{n,\alpha}\rangle$ with $\langle \Psi^{(0)}_{n,\alpha} | \mathbf{x} | \Psi^{(0)}_{n,\alpha} \rangle \neq 0$.

Quadratic Stark effect and the static polarizability tensor

Second order perturbation theory yields the following corrections to discrete atomic or molecular energy levels,

$$\begin{aligned} E^{(2)}_{n\alpha} &= \sum\!\!\!\!\!\!\int_{m \neq n} \sum_{\beta} \frac{|\langle \Psi^{(0)}_{m\beta} | V | \Psi^{(0)}_{n\alpha} \rangle|^2}{E^{(0)}_n - E^{(0)}_m} \\ &= q^2 \boldsymbol{E} \cdot \sum\!\!\!\!\!\!\int_{m \neq n} \sum_{\beta} \frac{\langle \Psi^{(0)}_{n\alpha} | \mathbf{x} | \Psi^{(0)}_{m\beta} \rangle \langle \Psi^{(0)}_{m\beta} | \mathbf{x} | \Psi^{(0)}_{n\alpha} \rangle}{E^{(0)}_n - E^{(0)}_m} \cdot \boldsymbol{E}. \end{aligned}$$

The notation takes into account that the intermediate levels can be continuous, but degeneracy indices are always discrete.

We can write the second order shifts in the form

$$E^{(2)}_{n\alpha} = -\frac{1}{2} \boldsymbol{d}_{(n\alpha)} \cdot \boldsymbol{E} = -\frac{1}{2} \boldsymbol{E} \cdot \underline{\alpha}_{(n\alpha)} \cdot \boldsymbol{E},$$

where

$$\boldsymbol{d}_{(n\alpha)} = \underline{\alpha}_{(n\alpha)} \cdot \boldsymbol{E}$$

is the *induced* dipole moment and $\underline{\alpha}_{(n\alpha)}$ is the static electronic polarizability tensor in the state $|\Psi^{(0)}_{n\alpha}\rangle$,

$$\begin{aligned} \underline{\alpha}_{(n\alpha)} = -q^2 \sum\!\!\!\!\!\!\int_{m \neq n} \sum_{\beta} \frac{1}{E^{(0)}_n - E^{(0)}_m} \Big(& \langle \Psi^{(0)}_{n\alpha} | \mathbf{x} | \Psi^{(0)}_{m\beta} \rangle \otimes \langle \Psi^{(0)}_{m\beta} | \mathbf{x} | \Psi^{(0)}_{n\alpha} \rangle \\ & + \langle \Psi^{(0)}_{m\beta} | \mathbf{x} | \Psi^{(0)}_{n\alpha} \rangle \otimes \langle \Psi^{(0)}_{n\alpha} | \mathbf{x} | \Psi^{(0)}_{m\beta} \rangle \Big). \end{aligned} \tag{15.21}$$

Note that in the ground state $\alpha_{ii} > 0$ (no summation convention), i.e. in second order perturbation theory, which usually should capture all linear contributions from a weak external electric field to the induced dipole moment, there is no electronic dia-electricity for the ground state.

15.3 Dynamical polarizability tensors

We cannot use time-independent perturbation theory if the perturbation operator $V(t) = -q\mathbf{x}\cdot\boldsymbol{E}(t)$ varies with time. Application of our results from Chapter 13 for time-dependent perturbations implies that the first order transition probability from a state $|m\rangle$ into a state $|n\rangle$ under the action of the electric field $\boldsymbol{E}(t)$ between times t' and t is proportional to[2]

$$P^{(1)}_{m\to n}(t,t') = \left|\frac{q}{\hbar}\int_{t'}^{t} d\tau\ \exp(\mathrm{i}\omega_{nm}\tau)\boldsymbol{E}(\tau)\cdot\langle n|\mathbf{x}|m\rangle\right|^2,$$

where

$$\omega_{nm} = \frac{1}{\hbar}(E_n - E_m)\,.$$

For $t' \to -\infty$, $t \to \infty$, this becomes in particular (see our previous results (13.28, 13.29))

$$P^{(1)}_{m\to n} = 2\pi\left|\frac{q}{\hbar}\boldsymbol{E}(\omega_{nm})\cdot\langle n|\mathbf{x}|m\rangle\right|^2,$$

i.e. long term action of an external electric field can induce a transition in first order between energy levels E_m and E_n only if the field contains a Fourier component of the corresponding frequency ω_{nm}.

However, at this time we are interested in the problem how equation (15.21) can be generalized to a dynamical polarizability in the presence of a time-dependent external field $\boldsymbol{E}(t)$.

Suppose the system was in the state $|\Psi^{(0)}_{n,\alpha}(0)\rangle \equiv |\Psi^{(0)}_{n,\alpha}\rangle$ at $t = 0$, when it begins to experience the effect of the electric field. The shift of the wave function $|\Psi^{(0)}_{n,\alpha}(t)\rangle$ under the influence of the external field is

$$\begin{aligned}|\Psi_{n,\alpha}(t)\rangle - |\Psi^{(0)}_{n,\alpha}(t)\rangle &= \Theta(t)\left[U(t) - U_0(t)\right]|\Psi^{(0)}_{n,\alpha}\rangle\\ &= \Theta(t)U_0(t)\left[U_0^{+}(t)U(t)U_0(0) - 1\right]|\Psi^{(0)}_{n,\alpha}\rangle\\ &= \Theta(t)U_0(t)\left[U_D(t) - 1\right]|\Psi^{(0)}_{n,\alpha}\rangle,\end{aligned}$$

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[2] Recall that $|S_{nm}|^2$ is a true transition probability only if the initial and final state are discrete, while otherwise it enters into decay rates or cross sections.

and the first order shift is therefore

$$\begin{aligned}
|\Psi^{(1)}_{n,\alpha}(t)\rangle &= -\frac{\mathrm{i}}{\hbar}\Theta(t)U_0(t)\int_0^t d\tau\, H_D(\tau)|\Psi^{(0)}_{n,\alpha}\rangle \\
&= -\frac{\mathrm{i}}{\hbar}\Theta(t)U_0(t)\int_0^t d\tau\, U_0^+(\tau)V(\tau)U_0(\tau)|\Psi^{(0)}_{n,\alpha}\rangle \\
&= -\frac{\mathrm{i}}{\hbar}\Theta(t)\int_0^t d\tau\, U_0(t-\tau)V(\tau)U_0(\tau)|\Psi^{(0)}_{n,\alpha}\rangle.
\end{aligned}$$

The *induced* dipole moment in the state $|\Psi^{(0)}_{n,\alpha}\rangle$ is then given in leading order by the first order terms (recall that the 0th order term corresponds to the *intrinsic* dipole moment (15.20))

$$\begin{aligned}
\boldsymbol{d}_{(n\alpha)}(t) &= \langle\Psi^{(0)}_{n,\alpha}(t)|q\mathbf{x}|\Psi^{(1)}_{n,\alpha}(t)\rangle + \langle\Psi^{(1)}_{n,\alpha}(t)|q\mathbf{x}|\Psi^{(0)}_{n,\alpha}(t)\rangle \\
&= q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\int_0^t d\tau\,\langle\Psi^{(0)}_{n,\alpha}|U_0^+(t)\mathbf{x}U_0(t-\tau)\mathbf{x}\cdot\boldsymbol{E}(\tau)U_0(\tau)|\Psi^{(0)}_{n,\alpha}\rangle \\
&\quad -q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\int_0^t d\tau\,\langle\Psi^{(0)}_{n,\alpha}|U_0^+(\tau)\mathbf{x}\cdot\boldsymbol{E}(\tau)U_0^+(t-\tau)\mathbf{x}U_0(t)|\Psi^{(0)}_{n,\alpha}\rangle.
\end{aligned}$$

This becomes after insertion of complete sets of unperturbed states in $U_0(t-\tau) = U_0(t)U_0^+(\tau)$ and $U_0^+(t-\tau) = U_0(\tau)U_0^+(t)$

$$\begin{aligned}
\boldsymbol{d}_{(n\alpha)}(t) &= q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\sum\!\!\!\!\!\!\int_{m,\beta}\int_0^t d\tau\,\exp[\mathrm{i}\omega_{nm}(t-\tau)]\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle \\
&\quad\times\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}\cdot\boldsymbol{E}(\tau)|\Psi^{(0)}_{n,\alpha}\rangle - q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\sum\!\!\!\!\!\!\int_{m,\beta}\int_0^t d\tau\,\exp[-\mathrm{i}\omega_{nm}(t-\tau)] \\
&\quad\times\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}\cdot\boldsymbol{E}(\tau)|\Psi^{(0)}_{m,\beta}\rangle\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle \\
&= \int_0^\infty d\tau\,\underline{\alpha}_{(n\alpha)}(t-\tau)\cdot\boldsymbol{E}(\tau),
\end{aligned} \tag{15.22}$$

with a dynamical polarizability tensor

$$\begin{aligned}
\underline{\alpha}_{(n\alpha)}(t) &= q^2\frac{\mathrm{i}}{\hbar}\Theta(t)\left(\sum\!\!\!\!\!\!\int_{m,\beta}\exp(\mathrm{i}\omega_{nm}t)\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\right. \\
&\quad\left.-\sum\!\!\!\!\!\!\int_{m,\beta}\exp(-\mathrm{i}\omega_{nm}t)\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\right).
\end{aligned} \tag{15.23}$$

Now we assume harmonic time dependence of an electric field which is switched on at $t = 0$,

$$\boldsymbol{E}(\tau) \equiv \boldsymbol{E}_\omega(\tau) = \boldsymbol{E}\Theta(t)\sin(\omega\tau) = \boldsymbol{E}\Theta(t)\,\frac{\exp(\mathrm{i}\omega\tau)-\exp(-\mathrm{i}\omega\tau)}{2\mathrm{i}}.$$

The time integrals in the two terms for $\boldsymbol{d}_{(n\alpha)}(t)$ then yield

$$\begin{aligned}
&\pm\frac{q^2}{2\hbar}\int_0^t d\tau\Big(\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)+\mathrm{i}\omega\tau]-\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)-\mathrm{i}\omega\tau]\Big)\\
&=\pm\frac{q^2}{2\mathrm{i}\hbar}\left(\frac{\exp(\mathrm{i}\omega t)-\exp(\pm\mathrm{i}\omega_{nm}t)}{\omega\mp\omega_{nm}}+\frac{\exp(-\mathrm{i}\omega t)-\exp(\pm\mathrm{i}\omega_{nm}t)}{\omega\pm\omega_{nm}}\right)\\
&=\pm\frac{q^2}{\mathrm{i}\hbar}\frac{\omega\cos(\omega t)\pm\mathrm{i}\omega_{nm}\sin(\omega t)-\omega\exp(\pm\mathrm{i}\omega_{nm}t)}{\omega^2-\omega_{nm}^2}.
\end{aligned}\tag{15.24}$$

We also assume slowly oscillating field in the sense $\omega \ll |\omega_{nm}|$ for all quantum numbers m which correspond to large matrix elements $|\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle|$. This means that the external field is not likely to induce direct transitions between different energy levels. Under these conditions, the contribution from the integrals in equation (15.24) to $\boldsymbol{d}_{(n\alpha)}(t)$ will be dominated by the term which is in phase with the external field,

$$\begin{aligned}
&\pm\frac{q^2}{2\hbar}\int_0^t d\tau\Big(\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)+\mathrm{i}\omega\tau]-\exp[\pm\mathrm{i}\omega_{nm}(t-\tau)-\mathrm{i}\omega\tau]\Big)\\
&\to\frac{q^2}{\hbar}\frac{\omega_{nm}\sin(\omega t)}{\omega^2-\omega_{nm}^2},
\end{aligned}$$

and the induced dipole moment in this approximation is

$$\begin{aligned}
\boldsymbol{d}_{(n\alpha)\omega}(t)=\frac{q^2}{\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{mn}}{\omega_{mn}^2-\omega^2}\Big(&\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}\cdot\boldsymbol{E}_\omega(t)|\Psi^{(0)}_{n,\alpha}\rangle\\
&+\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}\cdot\boldsymbol{E}_\omega(t)|\Psi^{(0)}_{m,\beta}\rangle\Big).
\end{aligned}$$

This can also be written as

$$\boldsymbol{d}_{(n\alpha)\omega}(t)=\underline{\alpha}_{(n\alpha)}(\omega)\cdot\boldsymbol{E}_\omega(t)$$

with the frequency dependent polarizability tensor for the state $|\Psi^{(0)}_{n,\alpha}\rangle$ (usually the ground state)

$$\begin{aligned}
\underline{\alpha}_{(n\alpha)}(\omega)=\frac{q^2}{\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{mn}}{\omega_{mn}^2-\omega^2}\Big(&\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\\
&+\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\Big).
\end{aligned}\tag{15.25}$$

The zero frequency polarizability tensor $\underline{\alpha}_{(n\alpha)}(0)$ is the static tensor (15.21), as expected.

The frequency dependent polarizability tensor is not only relevant for slowly oscillating fields, but appears implicitly already in the equations (15.22, 15.23), which do not include a restriction to slowly oscillating external field. If we agree to shift the denominator in (15.25) by small imaginary numbers according to

$$\begin{aligned}\underline{\alpha}_{(n\alpha)}(\omega) = \frac{q^2}{\hbar}\Bigg(&\sum\!\!\!\!\!\!\int_{m,\beta} \frac{\omega_{nm}}{\omega^2-\omega_{nm}^2-\mathrm{i}\epsilon}\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\\ &+\sum\!\!\!\!\!\!\int_{m,\beta} \frac{\omega_{nm}}{\omega^2-\omega_{nm}^2+\mathrm{i}\epsilon}\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\Bigg), \quad (15.26)\end{aligned}$$

we find that the dynamical polarizability tensors in equations (15.23) and (15.26) are related via

$$\underline{\alpha}_{(n\alpha)}(t) = \frac{\Theta(t)}{\pi}\int_{-\infty}^{\infty}d\omega\,\underline{\alpha}_{(n\alpha)}(\omega)\exp(-\mathrm{i}\omega t). \quad (15.27)$$

Oscillator strength

Equation (15.26) yields an averaged polarizability

$$\begin{aligned}\alpha_{(n\alpha)}(\omega) &= \frac{1}{3}\mathrm{tr}\,\underline{\alpha}_{(n\alpha)}(\omega) = \frac{2q^2}{3\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{\omega_{mn}}{\omega_{mn}^2-\omega^2}|\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle|^2\\ &= \frac{q^2}{m}\sum\!\!\!\!\!\!\int_{m,\beta}\frac{f_{m,\beta;n,\alpha}}{\omega_{mn}^2-\omega^2}\end{aligned}$$

with the *oscillator strength* for the transition $|\Psi^{(0)}_{n,\alpha}\rangle \to |\Psi^{(0)}_{m,\beta}\rangle$:

$$f_{m,\beta;n,\alpha} = \frac{2m}{3\hbar}\omega_{mn}|\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle|^2 = -f_{n,\alpha;m,\beta}. \quad (15.28)$$

We use m both for the mass of the charged (quasi)particle which has its wave functions shifted due to the external field, and as a label for the intermediate states. Since mass never appears as an index in equation (15.28) or the following equations, this should not cause confusion.

The polarizability is also often averaged over degenerate initial states. If the degeneracy of the n-th energy level is g_n, then

$$\alpha_n(\omega) = \frac{1}{g_n}\sum_{\alpha}\alpha_{(n\alpha)}(\omega) = \frac{q^2}{m}\sum\!\!\!\!\!\!\int_{m}\frac{f_{m|n}}{\omega_{mn}^2-\omega^2}$$

with an effective oscillator strength which is averaged over degenerate initial states and summed over degenerate final states,

$$f_{m|n} = \frac{1}{g_n}\sum_{\alpha,\beta}f_{m,\beta;n,\alpha} = -\frac{g_m}{g_n}f_{n|m}. \quad (15.29)$$

With these conventions, positive oscillator strength corresponds to absorption and negative oscillator strength corresponds to emission. Oscillator strengths are sometimes also defined through absolute values, but for the f-sum rules below it plays a role that emission transitions contribute with negative sign.

For an explanation of the name *oscillator strength* for $f_{m,\beta;n,\alpha}$, we observe that a classical isotropic harmonic oscillator model for polarizability

$$m\ddot{\boldsymbol{x}}(t) + m\omega_0^2\boldsymbol{x}(t) = q\boldsymbol{E}\sin(\omega t)$$

yields an induced dipole moment

$$\boldsymbol{d}_\omega(t) = q\boldsymbol{x}(t) = \frac{q^2}{m}\frac{1}{\omega_0^2 - \omega^2}\boldsymbol{E}\sin(\omega t) = \alpha(\omega)\boldsymbol{E}_\omega(t)$$

with the polarizability

$$\alpha(\omega) = \frac{q^2}{m}\frac{1}{\omega_0^2 - \omega^2},$$

i.e. every virtual transition $|\Psi_{n,\alpha}^{(0)}\rangle \to |\Psi_{m,\beta}^{(0)}\rangle$ contributes effectively like an oscillator of frequency $|\omega_{mn}| = \left|E_m^{(0)} - E_n^{(0)}\right|/\hbar$ to the polarizability $\alpha_{(n\alpha)}(\omega)$ of the state $|\Psi_{n,\alpha}^{(0)}\rangle$, but the contribution of that transition is weighted with the oscillator strength (15.28).

Thomas-Reiche-Kuhn sum rule (f-sum rule) for the oscillator strength

Kuhn, Reiche and Thomas found a sum rule for the oscillator strength already in the framework of old quantum theory[3]. The quantum mechanical proof is based on the fact that the Hamiltonian operator $H = (\mathbf{p}^2/2m) + V(\mathbf{x})$ yields a commutator

$$[H, \mathbf{x}] = \frac{\hbar\mathbf{p}}{\mathrm{i}m}. \tag{15.30}$$

This implies for a discrete normalized state $|\Psi_{n,\alpha}^{(0)}\rangle$

$$\begin{aligned}\sum\!\!\!\!\!\!\int_{m,\beta} f_{m,\beta;n,\alpha} &= \frac{2m}{3\hbar}\sum\!\!\!\!\!\!\int_{m,\beta}\omega_{mn}\langle\Psi_{n,\alpha}^{(0)}|\mathbf{x}|\Psi_{m,\beta}^{(0)}\rangle\cdot\langle\Psi_{m,\beta}^{(0)}|\mathbf{x}|\Psi_{n,\alpha}^{(0)}\rangle \\ &= \frac{2m}{3\hbar^2}\sum\!\!\!\!\!\!\int_{m,\beta}\left(E_m^{(0)} - E_n^{(0)}\right)\langle\Psi_{n,\alpha}^{(0)}|\mathbf{x}|\Psi_{m,\beta}^{(0)}\rangle\cdot\langle\Psi_{m,\beta}^{(0)}|\mathbf{x}|\Psi_{n,\alpha}^{(0)}\rangle\end{aligned}$$

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[3] W. Kuhn, Z. Phys. 33, 408 (1925); F. Reiche, W. Thomas, Z. Phys. 34, 510 (1925).

$$= \frac{m}{3\hbar^2}\sum\!\!\!\!\!\!\!\int_{m,\beta}\Big(\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\cdot\langle\Psi^{(0)}_{m,\beta}|[H_0,\mathbf{x}]|\Psi^{(0)}_{n,\alpha}\rangle$$

$$-\langle\Psi^{(0)}_{n,\alpha}|[H_0,\mathbf{x}]|\Psi^{(0)}_{m,\beta}\rangle\cdot\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\Big)$$

$$= \frac{1}{3\mathrm{i}\hbar}\sum\!\!\!\!\!\!\!\int_{m,\beta}\Big(\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\cdot\langle\Psi^{(0)}_{m,\beta}|\mathbf{p}|\Psi^{(0)}_{n,\alpha}\rangle$$

$$-\Big\langle\Psi^{(0)}_{n,\alpha}|\mathbf{p}|\Psi^{(0)}_{m,\beta}\rangle\cdot\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\Big)$$

$$= \frac{1}{3\mathrm{i}\hbar}\langle\Psi^{(0)}_{n,\alpha}|(\mathbf{x}\cdot\mathbf{p}-\mathbf{p}\cdot\mathbf{x})|\Psi^{(0)}_{n,\alpha}\rangle = 1.$$

This is the[4] *Thomas-Reiche-Kuhn sum rule*,

$$\sum\!\!\!\!\!\!\!\int_{m,\beta} f_{m,\beta;n,\alpha} = 1. \tag{15.31}$$

Averaging over initial degeneracy indices (15.29) then also yields

$$\sum\!\!\!\!\!\!\!\int_{m} f_{m|n} = 1. \tag{15.32}$$

Equation (15.30) implies a further relation which connects matrix elements of $\mathbf{x}$ and $\mathbf{p}$,

$$\omega_{mn}\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle = \frac{1}{\mathrm{i}m}\langle\Psi^{(0)}_{m,\beta}|\mathbf{p}|\Psi^{(0)}_{n,\alpha}\rangle.$$

This yields an alternative representation of the oscillator strength

$$f_{m,\beta;n,\alpha} = \frac{2}{3m\hbar\omega_{mn}}|\langle\Psi^{(0)}_{m,\beta}|\mathbf{p}|\Psi^{(0)}_{n,\alpha}\rangle|^2, \tag{15.33}$$

which is known as the *velocity form* of the oscillator strength, while equation (15.28) is denoted as the *length form* of the oscillator strength. Yet another common definition in atomic, molecular and optical physics is

$$f_{m,\beta;n,\alpha} = \frac{2m\omega_{mn}}{3\hbar q^2}\mathcal{S}_{m,\beta;n,\alpha}, \quad f_{m|n} = \frac{2m\omega_{mn}}{3\hbar q^2}\mathcal{S}_{m,n},$$

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[4] If the wave functions are N-particle wave functions and the potential V is the corresponding sum of dipole operators, the number on the right hand side of the sum rules becomes N.

with the *electric dipole line strength* of the transition $|\Psi^{(0)}_{n,\alpha}\rangle \to |\Psi^{(0)}_{m,\beta}\rangle$

$$\begin{aligned}
\mathcal{S}_{m,\beta;n,\alpha} &= |\langle\Psi^{(0)}_{m,\beta}|q\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle|^2 = \left|\frac{q}{m\omega_{mn}}\langle\Psi^{(0)}_{m,\beta}|\mathbf{p}|\Psi^{(0)}_{n,\alpha}\rangle\right|^2, \\
\mathcal{S}_{m,n} &= \frac{1}{g_n}\sum_{\alpha,\beta}\mathcal{S}_{m,\beta;n,\alpha} = \frac{g_m}{g_n}\mathcal{S}_{n,m}.
\end{aligned}$$

Tensorial oscillator strengths and sum rules

We can define oscillator strength tensors through the relations

$$\begin{aligned}
\underline{\alpha}_{(n\alpha)}(\omega) &= \frac{q^2}{m}\sum_{m,\beta}\frac{\underline{f}_{m,\beta;n,\alpha}}{\omega_{mn}^2-\omega^2}, \\
\underline{\alpha}_n(\omega) &= \frac{1}{g_n}\sum_{\alpha}\underline{\alpha}_{(n\alpha)}(\omega) = \frac{q^2}{m}\sum_{m}\frac{\underline{f}_{m,n}}{\omega_{mn}^2-\omega^2},
\end{aligned}$$

i.e. we have representations for oscillator strength tensors

$$\begin{aligned}
\underline{f}_{m,\beta;n,\alpha} &= \frac{m}{\hbar}\omega_{mn}\Big(\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle \\
&\quad + \langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\Big) \\
&= \frac{m}{2\hbar^2}\Big(\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|[H_0,\mathbf{x}]|\Psi^{(0)}_{n,\alpha}\rangle \\
&\quad - \langle\Psi^{(0)}_{n,\alpha}|[H_0,\mathbf{x}]|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle \\
&\quad + \langle\Psi^{(0)}_{m,\beta}|[H_0,\mathbf{x}]|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle \\
&\quad - \langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|[H_0,\mathbf{x}]|\Psi^{(0)}_{m,\beta}\rangle\Big) \\
&= \frac{1}{2\mathrm{i}\hbar}\Big(\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{p}|\Psi^{(0)}_{n,\alpha}\rangle - \langle\Psi^{(0)}_{n,\alpha}|\mathbf{p}|\Psi^{(0)}_{m,\beta}\rangle\otimes\langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle \\
&\quad + \langle\Psi^{(0)}_{m,\beta}|\mathbf{p}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{x}|\Psi^{(0)}_{m,\beta}\rangle - \langle\Psi^{(0)}_{m,\beta}|\mathbf{x}|\Psi^{(0)}_{n,\alpha}\rangle\otimes\langle\Psi^{(0)}_{n,\alpha}|\mathbf{p}|\Psi^{(0)}_{m,\beta}\rangle\Big) \\
&= -\underline{f}_{n,\alpha;m,\beta},
\end{aligned} \tag{15.34}$$

and reduced oscillator strength tensors

$$\underline{f}_{m|n} = \frac{1}{g_n}\sum_{\alpha,\beta}\underline{f}_{m,\beta;n,\alpha} = -\frac{g_m}{g_n}\underline{f}_{n|m}. \tag{15.35}$$

This yields tensorial f-sum rules,

$$\sum_{m,\beta}\underline{f}_{m,\beta;n,\alpha} = \frac{1}{2\mathrm{i}\hbar}\langle\Psi^{(0)}_{n,\alpha}|\big([\mathrm{x}_i,\mathrm{p}_j]-[\mathrm{p}_i,\mathrm{x}_j]\big)|\Psi^{(0)}_{n,\alpha}\rangle\boldsymbol{e}_i\otimes\boldsymbol{e}_j = \underline{1} = \sum_m \underline{f}_{m|n}.$$

For comparison, we note that the polarization tensor of an isotropic classical oscillator is easily shown to be

$$\underline{\alpha}(\omega) = \frac{q^2}{m}\frac{1}{\omega_0^2-\omega^2}\underline{1}.$$

The standard oscillator strength is related to the oscillator strength tensor via

$$f_{m,\beta;n,\alpha} = \frac{1}{3}\mathrm{tr}\underline{f}_{m,\beta;n,\alpha}.$$

15.4 Problems

15.1. Show that the probability current density in the presence of electromagnetic potentials is given by

$$\boldsymbol{j} = \frac{\hbar}{2\mathrm{i}m}\left(\Psi^+\nabla\Psi - \nabla\Psi^+\cdot\Psi - 2\mathrm{i}\frac{q}{\hbar}\Psi^+\boldsymbol{A}\Psi\right).$$

Is this expression gauge invariant?

15.2. Suppose that a particle is moving in a spatially homogeneous magnetic field $\boldsymbol{B}(t)$. Show that in order $|q\boldsymbol{B}|$ this yields the Zeeman term

$$\langle\boldsymbol{x}|H_Z(t)|\Psi(t)\rangle = -\langle\boldsymbol{x}|\frac{q}{2m}\boldsymbol{B}(t)\cdot\boldsymbol{l}|\Psi(t)\rangle = \mathrm{i}\frac{q\hbar}{2m}\boldsymbol{B}(t)\cdot(\boldsymbol{x}\times\nabla)\Psi(\boldsymbol{x},t)$$

in the Schrödinger equation (15.6).

Hint: You can use equation (15.13).

15.3. A hydrogen atom is initially in its ground state when it is excited by an external electric field $\boldsymbol{E}(t)$.

15.3a. Show through direct evaluation of the matrix elements that the dipole term $V(t) = -q\mathbf{x}\cdot\boldsymbol{E}(t)$ in first order only excites higher level p states.

15.3b. The external field is

$$\boldsymbol{E}(t) = \boldsymbol{e}_z\mathcal{E}\exp(-t^2/\tau^2). \qquad (15.36)$$

How large are the first order transition probabilities $P_{1\to n}$ into excited bound energy levels?

15.4. How large is the ionization probability for a hydrogen atom in the electric field (15.36) in leading order perturbation theory?

15.5. Calculate the ionization probability (13.40) for a hydrogen atom in its ground state which is perturbed by an oscillating electric field in z direction,

$$V(t) = ez\mathcal{E}\cos(\omega t).$$

15.6. Calculate the linear Stark effect for the first excited level of hydrogen due to a homogeneous static electric field $\boldsymbol{E}$.

15.7. Calculate the static polarizability tensor in the ground state of hydrogen.

15.8. Calculate the oscillator strengths $f_{n';n} = 2m\omega_{n'n}|\langle n'|x|n\rangle|^2/\hbar$ for a one-dimensional oscillator. Why does the equation for the one-dimensional oscillator strength differ by a factor 3 from the three-dimensional oscillator strength (15.28)?

15.9. Calculate the oscillator strengths $f_{n,\ell,m;1,0,0}$ for the hydrogen atom. How large is the sum

$$\sum_{\ell=0}^{\infty}\sum_{m=-\ell}^{\ell}\int_0^{\infty} dk\, k^2 f_{k,\ell,m;1,0,0}$$

of the oscillator strengths into Coulomb waves?

15.10. We consider the transition $|m\rangle \to |n\rangle$ due to an external electric field $\boldsymbol{E}(t)$. Show that the square of the corresponding first order scattering matrix element is related to the oscillator strength tensor of the transition through

$$|S_{nm}|^2 = \frac{\pi q^2}{m\hbar\omega_{nm}}\boldsymbol{E}(\omega_{nm})\cdot\underline{f}_{n;m}\cdot\boldsymbol{E}(\omega_{nm}).$$

15.11. Show that normalizable energy eigenstates, $\langle n|n\rangle = 1$, have vanishing momentum expectation values,

$$\langle n|\mathbf{p}|n\rangle = 0.$$

Why does this equation not hold for plane wave states?

15.12. Prove the *Bethe sum rule*[5],

$$\frac{2m}{\hbar}\sum_{m,\beta}\omega_{mn}\left|\langle\Psi_{m,\beta}^{(0)}|\exp(\mathrm{i}\boldsymbol{k}\cdot\mathbf{x})|\Psi_{n,\alpha}^{(0)}\rangle\right|^2 = \boldsymbol{k}^2.$$

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[5] H. Bethe, Annalen Phys. 397, 325 (1930).