E
Fourier Transformations

E.1
Definition and General Properties

Consider a sufficiently smooth function f of one real (or complex) variable x,

$$f : \begin{cases} \mathbb{R} \rightarrow \mathbb{R} \\ x \mapsto f(x) \end{cases} \tag{E.1}$$

In many situations in mathematics, physics and chemistry it is advantageous to consider not the function f itself but a somehow transformed variant $\tilde{f}$ of the function f. The so-called *Fourier transform* or *Fourier transformation* (FT) of the function f is defined as

$$\tilde{f}(k) \;=\; \int_{-\infty}^{\infty} \mathrm{d}x\, e^{-\mathrm{i}kx} f(x) \;=\; \int \mathrm{d}x\, e^{-\mathrm{i}kx} f(x) \tag{E.2}$$

It is essential to note that f and $\tilde{f}$ are two different functions and not merely the same function depending on two different variables. For the sake of simplicity this distinction is not always reflected by the notation; however, we will explicitly distinguish these two functions by the $\tilde{f}$-notation in this appendix. Furthermore, since all integrals in this appendix extend over the whole real line it is convenient to not explicitly write down the limits of integration, which has been done in the second step of Eq. (E.2). Given the transformed function $\tilde{f}$ it is always possible to extract the original function f by a so-called *Fourier back transformation* (FBT) defined by

$$f(x) \;=\; \frac{1}{2\pi} \int \mathrm{d}k\, e^{+\mathrm{i}kx} \tilde{f}(k) \tag{E.3}$$

It is easy to see that the expressions for the two transformations (FT and FBT) are perfectly consistent with each other if and only if the integral representa-

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tion of Dirac's delta-function as given by Eq. (A.29) holds,

$$f(x) \overset{(E.3)}{=} \frac{1}{2\pi}\int dk\, e^{+ikx}\tilde{f}(k) \overset{(E.2)}{=} \int dx' \underbrace{\frac{1}{2\pi}\int dk\, e^{ik(x-x')}}_{\delta(x-x')} f(x')$$
$$\overset{(A.28)}{=} f(x) \tag{E.4}$$

Because of this feature Eq. (E.3) is also known as the *Fourier reciprocity theorem*.

We now investigate the Fourier transformation of the derivative $f' = df/dx$ of a function f. According to Eq. (E.2) it is given by

$$\widetilde{f'}(k) = \int dx\, e^{-ikx}\left[\frac{d}{dx}f(x)\right] \overset{(p.I.)}{=} -\int dx \left[\frac{d}{dx}e^{-ikx}\right] f(x)$$
$$= ik\int dx\, e^{-ikx}f(x) = ik\tilde{f}(k) \tag{E.5}$$

where integration by parts (p.I.) has been employed at the second equality. The surface term necessarily has to vanish for any integrable function f and has thus been neglected. We have derived the very important result that a derivative operator in normal (position) space reduces to a simple multiplicative operator in Fourier (momentum) space. Especially in quantum mechanics (cf. chapter 4) this feature is often conveniently exploited.

For the discussion of the Douglas–Kroll–Hess transformation in chapter 12 the Fourier transformation of a product of two functions, $h(x) = f(x)g(x)$, has been employed. In one dimension it is given by the convolution integral of the Fourier transformations of f and g,

$$\tilde{h}(k) = \int dx\, e^{-ikx}f(x)g(x) = \int dx\int dx'\, e^{-ikx}\,\delta(x-x')\,f(x)g(x')$$
$$\overset{(A.29)}{=} \int dx\int dx'\, e^{-ikx}\,\frac{1}{2\pi}\int dk' e^{ik'(x-x')}f(x)g(x')$$
$$= \frac{1}{2\pi}\int dk'\int dx\, e^{-i(k-k')x}f(x)\int dx' e^{-ik'x'}g(x')$$
$$= \frac{1}{2\pi}\int dk'\tilde{f}(k-k')\tilde{g}(k') \tag{E.6}$$

The formulae for Fourier transformations in three (or more) dimensions are straightforward generalizations of the one-dimensional formulae presented above and are thus not explicitly given in this appendix.

E.2
Fourier Transformation of the Coulomb Potential

The Coulomb potential, or more precisely, the Coulomb potential energy V between two charged particles with charges q_1 and q_2 in three dimensions in position-space (**r**-space) representation is given by

$$V(\boldsymbol{r}) = \frac{q_1 q_2}{|\boldsymbol{r}|} = \frac{q_1 q_2}{r} \tag{E.7}$$

where $r = |\boldsymbol{r}|$ denotes the spatial distance between the two charges. If q_1 and q_2 feature the same sign, i.e., either both charges are positive or negative, the potential will be repulsive, otherwise it will be negative and thus attractive.

For the discussion of the Douglas–Kroll–Hess transformation in chapter 12 it has been advantageous to consider the momentum-space representation of the Coulomb potential, which may be obtained via a Fourier transformation of $V(\boldsymbol{r})$. It is given by

$$\tilde{V}(\boldsymbol{k}) = \int d^3 r\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}} V(\boldsymbol{r}) \tag{E.8}$$

However, Eq. (E.8) cannot be evaluated directly in a straightforward manner. We thus introduce a suitable *cutoff* which damps the Coulomb potential sufficiently and define the family of cutoff potentials

$$V_\mu(\boldsymbol{r}) = \frac{q_1 q_2}{r} e^{-\mu r}, \qquad \forall \mu > 0 \tag{E.9}$$

Obviously $V_\mu(\boldsymbol{r}) \to V(\boldsymbol{r})$ for $\mu \to 0$.

Now we can try to calculate the Fourier transformation of $V_\mu(\boldsymbol{r})$. It is given by

$$\begin{aligned} \widetilde{V_\mu}(\boldsymbol{k}) &= q_1 q_2 \int d^3 r\, e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, V_\mu(\boldsymbol{r}) = q_1 q_2 \int d^3 r\, \frac{e^{-i\boldsymbol{k}\cdot\boldsymbol{r}}\, e^{-\mu r}}{r} \\ &= 2\pi\, q_1 q_2 \int_0^\infty dr \int_0^\pi d\theta\, r^2 \sin\theta\, \frac{e^{-ikr\cos\theta}\, e^{-\mu r}}{r} \end{aligned} \tag{E.10}$$

where we have introduced spherical polar coordinates in the last step with $\theta = \angle(\boldsymbol{k}, \boldsymbol{r})$. If we now introduce the substitution

$$x = \cos\theta \quad \Longrightarrow \quad dx = -\sin\theta\, d\theta \tag{E.11}$$

with $x(\theta = 0) = +1$ and $x(\theta = \pi) = -1$, we arrive at

$$\begin{aligned} \widetilde{V_\mu}(\boldsymbol{k}) &= 2\pi\, q_1 q_2 \int_0^\infty dr\, r e^{-\mu r} \int_{-1}^{+1} dx\, e^{-ikrx} \\ &= \frac{2\pi\, q_1 q_2}{-ik} \int_0^\infty dr\, e^{-\mu r} \left(e^{-ikr} - e^{ikr} \right) \\ &= \frac{2\pi i\, q_1 q_2}{k} \int_0^\infty dr \left(e^{-(\mu+ik)r} - e^{-(\mu-ik)r} \right) \\ &= \frac{2\pi i\, q_1 q_2}{k} \left(\frac{1}{\mu + ik} - \frac{1}{\mu - ik} \right) = \frac{4\pi\, q_1 q_2}{\mu^2 + k^2} \end{aligned} \tag{E.12}$$

For $\mu \to 0$ we finally arrive at the momentum-space representation of the Coulomb potential,

$$\tilde{V}(\boldsymbol{k}) = \lim_{\mu \to 0} \widetilde{V_\mu}(\boldsymbol{k}) = \frac{4\pi q_1 q_2}{k^2} \tag{E.13}$$

The Coulomb potential thus features a $1/k^2$-dependence in momentum space.