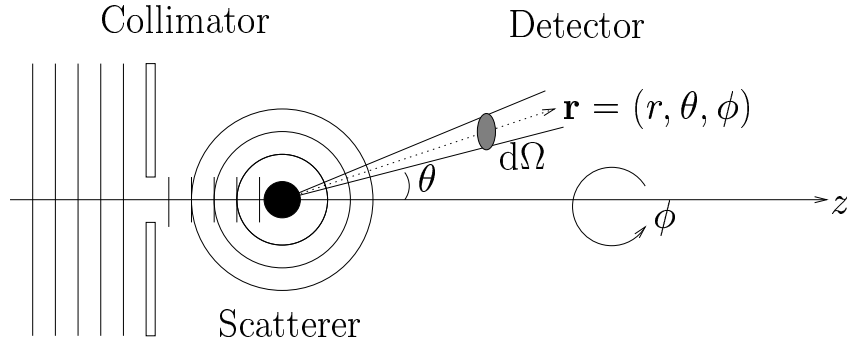# Inelastic scattering

Tony Paxton

Here are some notes from when I implemented the matrix elements for EELS and XANES in the LMTO code. It's mostly taken from Bethe and Roman, with many enjoyable discussions with Tchavdar Todorov.

Notes on inelastic scattering of electrons (EELS)

1. Geometry and definitions

The experimental set-up is shown in the figure. A narrow, collimated beam of electrons in plane waves states with wavevector $\mathbf{k}_i = k_z \equiv k$ scatters at an atom at the origin. The rate of scattering into the solid angle $\mathrm{d}\Omega$ is measured by the detector at $\mathbf{r}$. We will make two assumptions:

1. The incident particle intensity is sufficiently low that they may be regarded as non interacting, but not so low that the detector statistics are poor.

2. The incident particle velocity is greater than $(Z/137)c$, where Z is the atomic number of the atom and c is the speed of light. This lower bound assures that the first Born approximation is valid; *ie*, that we can use first order perturbation theory. To avoid relativistic corrections we also have an upper bound of about $\frac{1}{2}c$ on the velocity. This restricts us to a rather narrow range of incident electron energies between $15Z^2\mathrm{eV}$ and 60keV. However, the upper bound is not restrictive; it will turn out that the final equation is also very nearly correct in the relativistic case.

The scattering by the atom is characterised by the scattering *cross section*, σ, which is defined by the equations

$$\sigma = \int \sigma(\theta, \phi)\mathrm{d}\Omega \tag{1.1}$$

and

$$\sigma(\theta, \phi) = \frac{\mathrm{d}\sigma}{\mathrm{d}\Omega} = \frac{I(\theta, \phi)}{I_0}. \tag{1.2}$$

$\sigma(\theta, \phi)$ is called the *differential scattering cross section* and equation (1.2) defines this in terms of I_0, the incident flux; and $I(\theta, \phi)$, the number of particles per unit time, scattered through the cone subtended by the detector at $\mathbf{r}$.

2. The incident flux, I_0

The incident flux can be calculated simply if we make assumption number 1. The equation of *continuity* of a flux of quantum mechanical particles is

$$\dot{P}(\mathbf{r}, t) + \nabla \cdot \mathbf{S}(\mathbf{r}, t) = 0,$$

where P is the particle probability density per unit volume:

$$P = \bar{\psi}(\mathbf{r})\psi(\mathbf{r})$$

and $\mathbf{S}$ is the probability current density (per unit time per unit area):

$$\mathbf{S} = \frac{\hbar}{2im}\left[\bar{\psi}\nabla\psi - \left(\nabla\bar{\psi}\right)\psi\right]. \tag{2.1}$$

Since we take our plane waves to be non interacting, we have

$$\psi(\mathbf{r}) = \mathcal{N}e^{i\mathbf{k}_i \cdot \mathbf{r}} = \mathcal{N}e^{ikz}. \tag{2.2}$$

Here $\mathcal{N}$ is a normalisation constant having units of $[\text{length}]^{-3/2}$. Then, using (2.1) we get

$$I_0 = S = \mathcal{N}^2 \frac{\hbar k}{m}. \tag{2.3}$$

3. The transition probability, $I(\theta, \phi)$; Fermi's golden rule

At the atomic scale, we write $I(\theta, \phi) = w_{i \to f}$, which is the transition probability per unit time from the initial state into the final state of the system (atom plus electron beam). We can work out $w_{i \to f}$ quite generally to first order, ie, in the first Born approximation, if we write the hamiltonian, H, for the system as an unperturbed part, H_0, plus a small perturbing part, H_1, responsible for the transitions between stationary states, $u_n(\mathbf{r}_1, \mathbf{r}_2 \ldots)$, which are eigenfunctions of H_0, with eigenvalues E_n:

$$H_0 u_n = E_n u_n.$$

The solutions, $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, t)$ of the Schrödinger equation

$$i\hbar\dot{\Psi} = H\Psi \tag{3.1}$$

can be expanded in the stationary states of H_0:

$$\Psi = \sum_n a_n u_n e^{-E_n t/\hbar}.$$

Putting this into the Schrödinger equation (3.1), multiplying from the left by a particular stationary state wavefunction u_f and integrating $\mathrm{d}\tau$, ie, all spatial coordinates of the electrons over all space, we obtain

$$i\hbar\dot{a}_f(t) = \sum_n H'_{fn} e^{i\omega_{fn}t} a_n(0), \tag{3.2}$$

where

$$H'_{fn} = \int \mathrm{d}\tau\, \bar{u}_f H_1 u_n, \tag{3.3}$$

and we have defined

$$\omega_{fn} = \frac{1}{\hbar}\left(E_f - E_n\right). \tag{3.4}$$

If the system is initially in the stationary state i, then

$$a_n(0) = \delta_{ni},$$

and putting this into (3.2) and integrating, we get

$$a_f(t) = -\frac{i}{\hbar}\int_{-\infty}^{t} H'_{fi}\, e^{i\omega_{fi}t'}\,\mathrm{d}t'.$$

The constant of integration is zero, since $a_f(-\infty) = 0$. If H' is independent of time except that is it 'switched on' at $t = 0$ and 'switched off' at t, then

$$a_f(t) = -\frac{H'_{fi}}{\hbar} \frac{e^{i\omega_{fi}t} - 1}{\omega_{fi}},$$

and

$$\left| a_f(t) \right|^2 = \frac{4}{\hbar^2} \left| H'_{fi} \right|^2 \frac{\sin^2 \frac{1}{2}\omega_{fi}t}{\omega_{fi}^2}. \tag{3.5}$$

This is the probability of transition to state f over the duration t of the experiment. We denote this $W_{i \to f}(t)$. For two reasons, we don't yet have $w_{i \to f}$.

1. The final state is expected to be one of a *continuum* of states in the energy range about E_f between $E_f - \frac{1}{2}dE$ and $E_f + \frac{1}{2}dE$. The *number* of such states is $\rho(E)\,dE$ and $\rho(E)$ is the density of states per unit energy.

2. We want the transition probability *per unit time*. However if we compute $\rho(E)W_{i \to f}/t$ we get involved in details of how the interaction is 'switched' on and off. Furthermore we want the states i and f to be sharp (*ie*, to have long lifetimes). Therefore what we want to compute is

$$w_{i \to f} = \lim_{t \to \infty} \frac{1}{t} \int_{E_f - \frac{1}{2}dE}^{E_f + \frac{1}{2}dE} W_{i \to f}(t)\,\rho(E)\,dE. \tag{3.6}$$

We now make a further assumption, namely that the density of states is a much more slowly varying function of energy than $W_{i \to f}$. We therefore take $\rho(E)$ outside the integral in (3.6), insert (3.5) for $W_{i \to f}$ to obtain

$$w_{i \to f} = \frac{2\pi}{\hbar}\rho(E) \left| H'_{fi} \right|^2 \lim_{t \to \infty} \frac{1}{\hbar} \int_{E_f - \frac{1}{2}dE}^{E_f + \frac{1}{2}dE} \left(\frac{2\sin^2 \frac{1}{2}\omega_{fi}t}{\pi \omega_{fi}^2 t} \right) dE. \tag{3.7}$$

We next invoke the identity

$$\lim_{\alpha \to \infty} \frac{\sin^2 x\alpha}{x^2 \alpha} = \pi\delta(x), \tag{3.8}$$

and $\delta(ax) = (1/a)\delta(x)$, to write, using (3.4)

$$\lim_{t \to \infty} \frac{1}{\hbar} \int_{E_f - \frac{1}{2}dE}^{E_f + \frac{1}{2}dE} \left(\frac{2\sin^2 \frac{1}{2}\omega_{fi}t}{\pi \omega_{fi}^2 t} \right) dE = \int_{E_f - \frac{1}{2}dE}^{E_f + \frac{1}{2}dE} \delta(E_f - E_i)\,dE.$$

As long as E_i is in the range $E_f - \frac{1}{2}dE$ to $E_f + \frac{1}{2}dE$, then this is numerically equal to one, otherwise it is zero. This expresses the approximate energy conservation in first order scattering. The actual range dE is determined by the uncertainty principle. Therefore as long as E_i is within this range, the limit in (3.7) is one, and we get the very simple expression,

$$w_{i \to f} = \frac{2\pi}{\hbar}\rho(E) \left| H'_{fi} \right|^2, \tag{3.9}$$

which is Fermi's Golden Rule, actually due to Dirac. Note that we have not made the one-electron approximation in the derivation, and (3.3) is an integration over all electron coordinates.

4. Elastic scattering
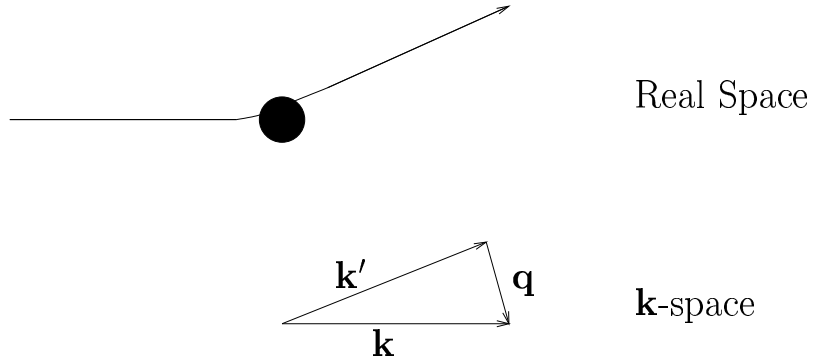
Suppose a beam of independent electrons with energy $\mathcal{E}$ is scattered elastically by a potential $V(\mathbf{r})$ at the origin. The situation is illustrated in the figure. This is now a one-electron problem.

We have

$$u_i(\mathbf{r}) = \mathcal{N}e^{i\mathbf{k}\cdot\mathbf{r}} \tag{4.1a}$$

$$u_f(\mathbf{r}) = \mathcal{N}e^{i(\mathbf{k}-\mathbf{q})\cdot\mathbf{r}} \tag{4.1b}$$

$\mathbf{q}$ is the momentum transfer. In this case, from (3.3)

$$H'_{fi} = \mathcal{N}^2 \int d\mathbf{r}\, V(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}} \equiv \mathcal{N}^2 M$$

and

$$w_{i\to f} = \frac{2\pi}{\hbar}\mathcal{N}^4\, |M|^2\, \rho(\mathcal{E}).$$

The number of independent electron states in the energy interval $d\mathcal{E}$ is, from the usual elementary argument,

$$\rho(\mathcal{E})d\mathcal{E} = \mathcal{N}^{-2}\left(\frac{k^2 dk}{8\pi^3}\right)$$

and using $\mathcal{E} = \hbar^2 k^2/2m$, we get

$$\rho(\mathcal{E}) = \mathcal{N}^{-2}\left(\frac{mk}{8\pi^3\hbar^2}\right).$$

The differential cross section is then, using (2.3),

$$\sigma(\theta,\phi) = \frac{w_{i\to f}}{I_0} = \left(\frac{m^2}{4\pi^2\hbar^4}\right)|M|^2.$$

Here, (θ,ϕ) describes the direction of the scattered beam $\mathbf{k}-\mathbf{q}$, and M is the scattering *matrix element*:

$$M(\mathbf{q}) = \int d\mathbf{r}\, V(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}}.$$

The normalisation constant cancels, as it should, since it is an arbitrarily chosen volume in the case of the scattering of an electron beam.

5. Elastic and inelastic scattering from an isolated atom

We imagine an electron with incident wavevector $\mathbf{k}_i$ and energy $\mathcal{E}_{\mathbf{k}_i} = \hbar^2 k_i^2 / 2m$ scattering at an isolated atom. We proceed as in section 3 to solve the Schrödinger equation (3.1); in which the hamiltonian now is

$$H = H_{\text{atom}} + H_{\text{electron}} + H_1,$$

where

$$H_1 = e^2 \left[\frac{Z}{r} - \sum_{j=1}^{Z} \frac{1}{\left| \mathbf{r} - \mathbf{r}_j \right|} \right].$$

This is the interaction hamiltonian between the incident electron, which is at position $\mathbf{r}$, and the atom whose nucleus is considered to be at rest at the origin. The second term is the Coulomb interaction between the incident electron and the Z atomic electrons at positions $\mathbf{r}_j$. The first term is the interaction with the nucleus; eventually this term will drop out in the calculation of the inelastic cross section. The wavefunction is now expanded in the eigenfunctions of $H_{\text{atom}} + H_{\text{electron}}$, which is H_0 the hamiltonian for the non interacting atom plus independent electron beam:

$$\Psi(\mathbf{r}, \mathbf{r}_1, \mathbf{r}_2, \ldots, t) = \sum_{n\mathbf{k}} a_n(\mathbf{k}, t) \, \psi_n(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_Z) \, \mathrm{e}^{i\mathbf{k}\cdot\mathbf{r}} \, \mathrm{e}^{-i(E_n + \mathcal{E}_{\mathbf{k}})t/\hbar}.$$

Here, $a_n(\mathbf{k}, t)$ is the expansion coefficent of the plane wave of wavevector $\mathbf{k}$ times the eigenfunction ψ_n of H_{atom} which has eigenvalue E_n. Then in exactly the way we obtained (3.2) we find

$$i\hbar \dot{a}_f(\mathbf{k}_f, t) = \sum_{n\mathbf{k}} T_{nf} \, \mathrm{e}^{i\omega_{fn}} \, a_n(\mathbf{k}, t)$$

where, with $\mathbf{q} = \mathbf{k} - \mathbf{k}_f$,

$$T_{nf} = \int \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \, \bar{\psi}_f \psi_n H_1 \, \mathrm{d}\mathbf{r}\mathrm{d}\tau,$$

and

$$\omega_{fn} = \frac{1}{\hbar} \left[(E_f + \mathcal{E}_{\mathbf{k}_f}) - (E_n + \mathcal{E}_{\mathbf{k}}) \right].$$

E_f and $\mathcal{E}_{\mathbf{k}_f}$ are the final state energies of the atom and electron. As before, we assert that the atom is intially in a state i so that

$$a_n(\mathbf{k}, 0) = \delta_{ni} \, \delta_{\mathbf{k}\mathbf{k}_i},$$

and the density of final states for the scattered electron beam is $\rho(\mathcal{E}_{\mathbf{k}_f})$. Exactly as before, as long as the conservation rule is adhered to, namely

$$(E_f + \mathcal{E}_{\mathbf{k}_f}) - (E_i + \mathcal{E}_{\mathbf{k}_i}) \approx 0,$$

where E_i is the initial state energy of the atom, we arrive at the Golden Rule (3.9):

$$w_{\text{i}\to\text{f}} = \frac{2\pi}{\hbar} \left| T_{if} \right|^2 \rho(\mathcal{E}_{\mathbf{k}_f})$$

where

$$T_{if} = e^2 \int \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \, \bar{\psi}_f \psi_i \left[\frac{Z}{r} - \sum_{j=1}^{Z} \frac{1}{\left| \mathbf{r} - \mathbf{r}_j \right|} \right] \mathrm{d}\mathbf{r} \, \mathrm{d}\tau.$$

One can manipulate T_{if} into a simpler expression by first integrating over the incident electron coordinate $\mathbf{r}$. We note that

$$e^{i\mathbf{q}\cdot\mathbf{r}} = -\frac{1}{q^2}\nabla^2 e^{i\mathbf{q}\cdot\mathbf{r}},$$

so that

$$\int e^{i\mathbf{q}\cdot\mathbf{r}}\left[\frac{Z}{r} - \sum_{j=1}^{Z}\frac{1}{\left|\mathbf{r}-\mathbf{r}_j\right|}\right]\mathrm{d}\mathbf{r} = -\frac{1}{q^2}\int e^{i\mathbf{q}\cdot\mathbf{r}}\left[\nabla^2\frac{Z}{r} - \sum_{j=1}^{Z}\nabla^2\frac{1}{\left|\mathbf{r}-\mathbf{r}_j\right|}\right]\mathrm{d}\mathbf{r}$$

$$= \frac{4\pi}{q^2}\int e^{i\mathbf{q}\cdot\mathbf{r}}\left[Z\delta(r) - \sum_{j=1}^{Z}\delta\left(\left|\mathbf{r}-\mathbf{r}_j\right|\right)\right]\mathrm{d}\mathbf{r}$$

$$= \frac{4\pi}{q^2}\left[Z - \sum_{j=1}^{Z}e^{i\mathbf{q}\cdot\mathbf{r}_j}\right].$$

The first line follows after two integrations by parts with the surface terms vanishing. We now have

$$T_{if} = \frac{4\pi e^2}{q^2}\int \bar{\psi}_f\psi_i\left[Z - \sum_{j=1}^{Z}e^{i\mathbf{q}\cdot\mathbf{r}_j}\right]\mathrm{d}\tau, \tag{5.1}$$

and the cross section for scattering is, following the arguments in section 3,

$$\sigma(\theta,\phi) = \left(\frac{m^2}{4\pi^2\hbar^4}\right)\frac{k_f}{k_i}\left|T_{if}\right|^2.$$

Note that this depends, through (5.1) on q^{-4} as in the classical Rutherford formula for scattering. It's not hard to see that in the case of elastic scattering, where $\psi_f = \psi_i$ (and $k_f = k_i$),

$$T_{if} = \frac{4\pi e^2}{q^2}[Z - F(\mathbf{q})]$$

where

$$F(\mathbf{q}) = \int \rho(\mathbf{r})\, e^{i\mathbf{q}\cdot\mathbf{r}}\,\mathrm{d}\mathbf{r}$$

is the Fourier transform of the atomic charge density, called the *form factor*. However for inelastic scattering the final and initial states are distinct and orthogonal so the first term in (5.1) integrates to zero. We therefore arrive at a central equation in these notes: Bethe's formula for the inelastic scattering differential cross section, [†]

$$\sigma(\theta,\phi) = \left(\frac{m^2}{4\pi^2\hbar^4}\right)\frac{k_f}{k_i}\left(\frac{4\pi e^2}{q^2}\right)^2\left|\int\bar{\psi}_f\psi_i\left[\sum_{j=1}^{Z}e^{i\mathbf{q}\cdot\mathbf{r}_j}\right]\mathrm{d}\mathbf{r}_1\mathrm{d}\mathbf{r}_2\ldots\mathrm{d}\mathbf{r}_Z\right|^2. \tag{5.2}$$

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[†] Actually Bethe derives a formula with relativistic corrections for the velocity of the incoming electron. His prefactor is

$$\left(\frac{m^2}{4\pi^2\hbar^4}\right)\frac{k_f}{k_i}\left(\frac{4\pi e^2}{q^2}\right)^2 = \left(\frac{2me^2}{\hbar^2q^2}\right)^2\frac{k_f}{k_i} \rightarrow \left(\frac{2e^2\mathcal{W}}{c^2\hbar^2q^2}\right)^2\frac{v_f}{v_i}$$

where v_i and v_f are initial and final electron velocities (and $k_f/k_i = v_f/v_i$) and $\mathcal{W}$ is the energy of the incoming electron including its rest mass. In these notes we have kept to the non relativistic case both for simplicity and because it turns out, as Bethe shows, that the final equation (5.4) is also relativistically "very nearly" correct.

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Next we want to find the partial cross section with respect to the magnitude of momentum transfer q rather than the scattering angles. To do this we first write (5.2) as

$$\sigma(\theta, \phi) = \left(\frac{m^2}{4\pi^2\hbar^4}\right) \frac{k_f}{k_i} \left(\frac{4\pi e^2}{q^2}\right)^2 \left|F_f(\mathbf{q})\right|^2$$

$$= \left(\frac{2me^2}{\hbar^2 q^2}\right)^2 \frac{k_f}{k_i} \left|F_f(\mathbf{q})\right|^2$$

which defines the *transition form factor* $F_f(\mathbf{q})$ for final state f. Then the cross section for inelastic scattering into final state f is, from (1.2),

$$\sigma_f = \left(\frac{2me^2}{\hbar^2}\right)^2 \frac{k_f}{k_i} \int d\Omega \, \frac{\left|F_f(\mathbf{q})\right|^2}{q^4}. \tag{5.3}$$

Now, $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$, $q^2 = \left(k_i - k_f\right)^2 + 4k_i k_f \sin \frac{1}{2}\theta$; $q\,dq = k_i k_f \sin\theta\,d\theta$. Therefore

$$\frac{k_f}{k_i}\,d\Omega = \frac{k_f}{k_i}\sin\theta\,d\theta\,d\phi = \frac{1}{k_i^2}\,q\,dq\,d\phi.$$

Putting this into (5.3) and doing the integral over ϕ brings out a factor of 2π and we are left with

$$\sigma_f = 2\pi \left(\frac{2e^2}{\hbar v_i}\right)^2 \int dq \, \frac{\left|F_f(\mathbf{q})\right|^2}{q^3},$$

where

$$v_i = \frac{\hbar k_i}{m}$$

is the group velocity of the incident electron beam (or wavepacket). Finally we get

$$\frac{d\sigma_f}{dq} = \left(\frac{8\pi e^4}{\hbar^2}\right) \frac{1}{v_i^2} \frac{1}{q^3} \left|F_f(\mathbf{q})\right|^2. \tag{5.4}$$

Equation (5.4) is also very nearly correct in the relativistic case $v_i > \frac{1}{2}c$. It is the starting point for our derivation of the EELS cross section, next.

6. Approximate formula for the differential cross section in EELS

Equation (5.4) is exact within the first Born approximation, but is as far as formal scattering theory can take us. Indeed Roman remarks,

> "Effects of target thickness, multiple scattering, cooperative phenomena in crystals, thermal motion, *etc.*, are considered as problems of instrumentation, outside the scope of the scattering theory proper."

This seems rather dismissive of KKR band theory, for one; but that's his view. Now in EELS, as opposed to the scattering from an isolated atom, the final state f is one of a continuum of band states labelled with a wavevector $\mathbf{k}$ and a band index n. (We no longer

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need $\mathbf{k}$ for the wavevector of the independent electron incoming and outgoing states, so there should be no confusion in notation). If we want to know what is the differential cross section with respect to momentum transfer for scattering into final states in the energy range $\mathrm{d}E$ around some energy E then from (5.4) we can infer this to be

$$\frac{\mathrm{d}\sigma(E,q)}{\mathrm{d}q} = \sum_{n\mathbf{k}} \frac{\mathrm{d}\sigma(q)}{\mathrm{d}q}\, \delta(E - E_{n\mathbf{k}})\, \mathrm{d}E,$$

and therefore the differential cross section with respect to both q and E is

$$\frac{\mathrm{d}^2\sigma(E,q)}{\mathrm{d}E\,\mathrm{d}q} = \sum_{n\mathbf{k}} \frac{\mathrm{d}\sigma(q)}{\mathrm{d}q}\, \delta(E - E_{n\mathbf{k}}). \tag{6.1}$$

We would like to insert (5.4) into this; but first we make two approximations. The first is the one-electron approximation which reduces the multiconfigurational integral for the transition form factor in (5.2) to

$$\begin{aligned}
F^{(1\mathrm{e})}_{n\mathbf{k}}(\mathbf{q}) &= \int \mathrm{d}\mathbf{r}\, \bar{\varphi}_{n\mathbf{k}}(\mathbf{r})\, \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}}\, \varphi_c(\mathbf{r}) \\
&= \left\langle n\mathbf{k} \left| \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \right| c \right\rangle.
\end{aligned}$$

Here, $\varphi_{n\mathbf{k}}(\mathbf{r}) = \langle \mathbf{r} \,|\, n\mathbf{k}\rangle$ is the band final state and $\varphi_c(\mathbf{r}) = \langle \mathbf{r} \,|\, c\rangle$ is the core initial state. We can remark here that the transition form factor can be written in this way as long as the states ψ_f and ψ_i can be approximated as Slater determinants. Because of the orthogonality of the orbitals, after taking the sum over j outside the integral, only one-electron integrals survive. On the other hand moving from the exact formula (5.4) to its one-electron approximation in this way removes all of the core-hole relaxation or "final state" effects. Since these are clearly absent therefore in the Hartree–Fock approximation, we can take these to be the consequence of electron correlations between the initial and final states ψ_f and ψ_i, rather than correlations between the incoming electron and the atomic states.[†] The only other possible origin of these effects is higher order scattering terms beyond the first Born approximation.

The second is called the *dipole approximation* because the exponential is expanded to first order as

$$\mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \approx 1 + i\mathbf{q}\cdot\mathbf{r}$$

and

$$\begin{aligned}
\left\langle n\mathbf{k} \left| \mathrm{e}^{i\mathbf{q}\cdot\mathbf{r}} \right| c \right\rangle &\approx \left\langle n\mathbf{k} \,|\, i\mathbf{q}\cdot\mathbf{r} \,|\, c \right\rangle \\
&= q \left\langle n\mathbf{k} \,|\, i\hat{\varepsilon}_{\mathbf{q}}\cdot\mathbf{r} \,|\, c \right\rangle
\end{aligned}$$

because the core state is orthogonal to the final state. Here, $\hat{\varepsilon}_{\mathbf{q}}$ is a unit vector in the direction of $\mathbf{q}$. The dipole approximation is admissible because of the q^{-4} dependence of the differential cross section in (5.1). It leads to the well known dipole selection rules arising from the matrix element

$$\begin{aligned}
M_d &= i\left\langle n\mathbf{k} \,|\, r \,|\, c \right\rangle \\
&= i\int \mathrm{d}\mathbf{r}\, \bar{\varphi}_{n\mathbf{k}}(\mathbf{r})\, r\, \varphi_c(\mathbf{r}). \tag{6.2}
\end{aligned}$$

[†] This last point can be made because whereas it is an approximation to write ψ_f and ψ_i as product functions or Slater determinants, the many-body wavefunction *is* a product of ψ_n and a plane-wave state in time-dependent perturbation theory.

Using these approximations, we put (5.4) into (6.1) and get

$$\frac{\mathrm{d}^2\sigma(E,q)}{\mathrm{d}E\,\mathrm{d}q} = \left(\frac{8\pi e^4}{\hbar^2 v_i^2}\right) \frac{1}{q} \sum_{n\mathbf{k}} |\langle n\mathbf{k}|\hat{\epsilon}_\mathbf{q}\cdot\mathbf{r}|c\rangle|^2 \, \delta(E - E_{n\mathbf{k}})$$

which is equation (4) in Muller, Singh and Silcox. If we average over all orientations of $\mathbf{q}$, which amounts to assuming specimen isotropy, then $\hat{\epsilon}_\mathbf{q}\cdot\mathbf{r}$ averages to $\frac{1}{3}r$ and we get, using (6.2),

$$\frac{\mathrm{d}^2\sigma(E,q)}{\mathrm{d}E\,\mathrm{d}q} = \left(\frac{8\pi e^4}{3\hbar^2 v_i^2 q}\right) \sum_{n\mathbf{k}} |M_d|^2 \, \delta(E - E_{n\mathbf{k}})$$

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