Momentum density-density correlations

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Total Hamiltonian

$$\hat{H} = \hat{H}_{\mathrm{mol}} + \hat{H}_{\mathrm{EM}} + \hat{H}_{\mathrm{int}}$$

Remarks:

- We work in the Schrödinger picture. Therefore, operators such as the vector potential are time-independent.
- For some x-ray applications, such as the one considered here, it is critical to avoid making the electric dipole approximation.

Molecular Hamiltonian

$$\hat{H}_{\mathrm{mol}} = \hat{T}_{\mathrm{N}} + \hat{V}_{\mathrm{NN}} + \hat{H}_{\mathrm{el}}$$

$$\hat{T}_{\mathrm{N}} = -\frac{1}{2}\sum_n \frac{\nabla_n^2}{M_n}$$

Kinetic energy of nuclei

$$\hat{V}_{\mathrm{NN}} = \sum_{n<n'} \frac{Z_n Z_{n'}}{|\boldsymbol{R}_n - \boldsymbol{R}_{n'}|}$$

Nucleus-nucleus repulsion

$$\hat{H}_{\mathrm{el}} = \int \mathrm{d}^3x \hat{\psi}^\dagger(\boldsymbol{x}) \left\{ -\frac{1}{2}\nabla^2 - \sum_n \frac{Z_n}{|\boldsymbol{x} - \boldsymbol{R}_n|} \right\} \hat{\psi}(\boldsymbol{x}) + \frac{1}{2}\int \mathrm{d}^3x \int \mathrm{d}^3x' \hat{\psi}^\dagger(\boldsymbol{x}) \hat{\psi}^\dagger(\boldsymbol{x}') \frac{1}{|\boldsymbol{x} - \boldsymbol{x}'|} \hat{\psi}(\boldsymbol{x}') \hat{\psi}(\boldsymbol{x})$$

Electronic Hamiltonian

$$\{\hat{\psi}_\sigma(\boldsymbol{x}), \hat{\psi}_{\sigma'}(\boldsymbol{x}')\} = 0,$$

$$\{\hat{\psi}_\sigma(\boldsymbol{x}), \hat{\psi}^\dagger_{\sigma'}(\boldsymbol{x}')\} = \delta_{\sigma,\sigma'}\delta^{(3)}(\boldsymbol{x} - \boldsymbol{x}'),$$

$$\{\hat{\psi}^\dagger_\sigma(\boldsymbol{x}), \hat{\psi}^\dagger_{\sigma'}(\boldsymbol{x}')\} = 0.$$

Anticommutator relations for electron field operators

Hamiltonian for free electromagnetic field

$$\hat{H}_{\mathrm{EM}} = \sum_{\boldsymbol{k},\lambda} \omega_{\boldsymbol{k}} \hat{a}^{\dagger}_{\boldsymbol{k},\lambda} \hat{a}_{\boldsymbol{k},\lambda}, \quad \omega_{\boldsymbol{k}} = |\boldsymbol{k}|/\alpha$$

$$[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}_{\boldsymbol{k}',\lambda'}] = 0,$$
$$[\hat{a}_{\boldsymbol{k},\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}',\lambda'}] = \delta_{\boldsymbol{k},\boldsymbol{k}'}\delta_{\lambda,\lambda'},$$
$$[\hat{a}^{\dagger}_{\boldsymbol{k},\lambda}, \hat{a}^{\dagger}_{\boldsymbol{k}',\lambda'}] = 0.$$

Commutator relations for photon mode operators

$$\hat{H}_{\mathrm{int}} = \alpha \int d^3x \hat{\psi}^{\dagger}(\boldsymbol{x}) \left[\hat{\boldsymbol{A}}(\boldsymbol{x}) \cdot \frac{\boldsymbol{\nabla}}{\mathrm{i}} \right] \hat{\psi}(\boldsymbol{x}) + \frac{\alpha^2}{2} \int d^3x \hat{\psi}^{\dagger}(\boldsymbol{x}) \hat{A}^2(\boldsymbol{x}) \hat{\psi}(\boldsymbol{x}),$$

Interaction between electrons and photons (minimal coupling, Coulomb gauge)

$$\hat{\boldsymbol{A}}(\boldsymbol{x}) = \sum_{\boldsymbol{k},\lambda} \sqrt{\frac{2\pi}{V\omega_{\boldsymbol{k}}\alpha^2}} \left\{ \hat{a}_{\boldsymbol{k},\lambda} \boldsymbol{\epsilon}_{\boldsymbol{k},\lambda} e^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} + \hat{a}^{\dagger}_{\boldsymbol{k},\lambda} \boldsymbol{\epsilon}^{*}_{\boldsymbol{k},\lambda} e^{-\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{x}} \right\}$$

Mode expansion of vector potential

$$\boldsymbol{k} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k},\lambda} = 0, \quad \boldsymbol{\epsilon}^{*}_{\boldsymbol{k},1} \cdot \boldsymbol{\epsilon}_{\boldsymbol{k},2} = 0.$$

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$$\hat{H} = \hat{H}_0 + \hat{H}_{\rm int}$$

$$\hat{H}_0 = \hat{H}_{\rm mol} + \hat{H}_{\rm EM}$$

Full Hamiltonian and unperturbed part

$$|I\rangle = |\Psi_0^{N_{\rm el}}\rangle |N_{\rm EM}\rangle$$

Initial state

Interaction-picture state vector to second order in perturbation

$$\begin{aligned} |\Psi, t\rangle_{\rm int} = |I\rangle - {\rm i} \int_{-\infty}^{t} {\rm d}t' {\rm e}^{{\rm i}\hat{H}_0 t'} \hat{H}_{\rm int} {\rm e}^{-\epsilon|t'|} {\rm e}^{-{\rm i}\hat{H}_0 t'} |I\rangle \\ - \int_{-\infty}^{t} {\rm d}t' {\rm e}^{{\rm i}\hat{H}_0 t'} \hat{H}_{\rm int} {\rm e}^{-\epsilon|t'|} {\rm e}^{-{\rm i}\hat{H}_0 t'} \int_{-\infty}^{t'} {\rm d}t'' {\rm e}^{{\rm i}\hat{H}_0 t''} \hat{H}_{\rm int} {\rm e}^{-\epsilon|t''|} {\rm e}^{-{\rm i}\hat{H}_0 t''} |I\rangle + \ldots \end{aligned}$$

Transition rate to second order in perturbation

$$\Gamma_{FI} = 2\pi\delta(E_F - E_I) \left| \langle F|\hat{H}_{\rm int}|I\rangle + \sum_M \frac{\langle F|\hat{H}_{\rm int}|M\rangle\langle M|\hat{H}_{\rm int}|I\rangle}{E_I - E_M + {\rm i}\epsilon} + \ldots \right|^2$$

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One-photon scattering via A² (one photon in, one photon out)

- Depends on the correlation functions

$$G^{(1)}(\vec{x}_1 t_1, \vec{x}_2 t_2), \langle \hat{n}(\vec{x}_1 t_1) \hat{n}(\vec{x}_2 t_2) \rangle$$

$$\hat{n}(\vec{x}t) = \hat{\psi}^\dagger(\vec{x}t)\hat{\psi}(\vec{x}t)$$

- "coherent": $\langle \hat{n}(\vec{x}_1 t_1) \rangle \langle \hat{n}(\vec{x}_2 t_2) \rangle = \langle \hat{n}(\vec{x}_1) \rangle \langle \hat{n}(\vec{x}_2) \rangle$

  sensitive to the electron density in real space, $\langle \hat{n}(\vec{x}) \rangle$

- "incoherent": $\sum_{F \neq 0} \langle \Psi_0 | \hat{n}(\vec{x}_1 t_1) | \Psi_F \rangle \langle \Psi_F | \hat{n}(\vec{x}_2 t_2) | \Psi_0 \rangle$

- $\langle \hat{n}(\vec{x}_1 t_1) \hat{n}(\vec{x}_2 t_2) \rangle$ can be used, for homogeneous systems (!), to reconstruct the real-space density propagator from linear-response theory

- The incoherent scattering signal, in the impulse approximation, is connected to the electron density in momentum space, $\langle \hat{n}(\vec{p}) \rangle$, which is NOT simply the Fourier transform of $\langle \hat{n}(\vec{x}) \rangle$

Opportunity: "Incoherent" A^2 two-photon scattering ("quantum photon correlation spectroscopy")

- Depends on

$$G^{(2)}(\vec{x}_1 t_1, \vec{x}_2 t_2, \vec{x}_3 t_3, \vec{x}_4 t_4), \langle \hat{n}(\vec{x}_1 t_1)\hat{n}(\vec{x}_2 t_2)\hat{n}(\vec{x}_3 t_3)\hat{n}(\vec{x}_4 t_4)\rangle$$

- Using a variant of the impulse approximation, it should be possible to connect this to the momentum-density autocorrelation function,

$$\langle \hat{n}(\vec{p}_1 t_1)\hat{n}(\vec{p}_2 t_2)\rangle$$

- I don't think there are other probes of this quantity. The details will have to be worked out.
- Requirements:
  - High intensity, permitting one to observe photon correlations
  - High monochromaticity and high detector energy resolution (particularly when focusing not exclusively on the Compton regime)
  - Degree of second-order coherence should equal unity (laser!)
  - Two detectors for coincidence measurements