Método variacional e amplitude de espalhamento

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Exercício 1

- Com as três definições da amplitude de espalhamento, podemos construir o seguinte funcional (em unidades atômicas)

$$[f(\mathbf{k_f}, \mathbf{k_i})] = -\frac{1}{2\pi}\left[\left\langle S_{\mathbf{k_f}} \middle| V \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle + \left\langle \Psi^{(-)}_{\mathbf{k_f}} \middle| V \middle| S_{\mathbf{k_i}} \right\rangle - \left\langle \Psi^{(-)}_{\mathbf{k_f}} \middle| A^{(+)} \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle \right]$$

- Fazendo variações de $\left|\Psi^{(+)}_{\mathbf{k_i}}\right\rangle$ independente de variações em $\left\langle\Psi^{(-)}_{\mathbf{k_f}}\right|$ em torno dos seus valores exatos, impondo que

$$\delta[f(\mathbf{k_f}, \mathbf{k_i})] = 0$$

obtemos

$$0 = \delta\left[\left\langle S_{\mathbf{k_f}} \middle| V \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle + \left\langle \Psi^{(-)}_{\mathbf{k_f}} \middle| V \middle| S_{\mathbf{k_i}} \right\rangle - \left\langle \Psi^{(-)}_{\mathbf{k_f}} \middle| A^{(+)} \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle \right]$$

ou ainda

$$0 = \left\langle S_{\mathbf{k_f}} \middle| V\delta \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle - \left\langle \Psi^{(-)}_{\mathbf{k_f}} \middle| A^{(+)}\delta \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle$$

- Ou seja

$$0 = \left[\langle S_{\mathbf{k_f}} \right| V - \left\langle \Psi^{(-)}_{\mathbf{k_f}} \right| A^{(+)} \left] \delta \left| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle \Rightarrow \left\langle \Psi^{(-)}_{\mathbf{k_f}} \right| A^{(+)} = \langle S_{\mathbf{k_f}} \right| V$$

- Se $A^{(+)\dagger} = A^{(-)}$

$$\boxed{A^{(-)} \left| \Psi^{(-)}_{\mathbf{k_f}} \right\rangle = V \left| S_{\mathbf{k_f}} \right\rangle}$$

- Semelhantemente para $\delta \left\langle \Psi^{(-)}_{\mathbf{k_f}} \right|$ independente de $\delta \left| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle$, podemos obter

$$\boxed{A^{(+)} \left| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle = V \left| S_{\mathbf{k_i}} \right\rangle}$$

Exercício 2

- Temos que

$$[f(\mathbf{k_f},\mathbf{k_i})] = -\frac{1}{2\pi}\left[\left\langle S_{\mathbf{k_f}}\middle|V\middle|\Psi^{(+)}_{\mathbf{k_i}}\right\rangle + \left\langle\Psi^{(-)}_{\mathbf{k_f}}\middle|V\middle|S_{\mathbf{k_i}}\right\rangle - \left\langle\Psi^{(-)}_{\mathbf{k_f}}\middle|A^{(+)}\middle|\Psi^{(+)}_{\mathbf{k_i}}\right\rangle\right] \quad (1)$$

- $|\Psi\rangle$ aparece sempre multiplicado por V, podemos expandir nossas funções de onda de espalhamento em uma base de funções L^2

$$\left|\Psi^{(\pm)}_{\mathbf{k_{i,f}}}\right\rangle = \sum_\mu a^{(\pm)}_\mu(\mathbf{k_{i,f}})\left|\chi_\mu\right\rangle \quad (2)$$

  com as seguintes definições

$$a^{(+)}_\mu(\mathbf{k_i}) = \left\langle\chi_\mu\middle|\Psi^{(+)}_{\mathbf{k_i}}\right\rangle \equiv a_\mu \equiv (\mathbf{a})_\mu \quad (3)$$

  e

$$a^{*(-)}_\nu(\mathbf{k_f}) = \left\langle\Psi^{(-)}_{\mathbf{k_f}}\middle|\chi_\nu\right\rangle \equiv \tilde{a}_\nu \equiv (\tilde{\mathbf{a}})_\nu \quad (4)$$

  se considerarmos $\sum_\mu \left|\chi_\mu\right\rangle\left\langle\chi_\mu\right| \approx \mathbb{1}$

- Notemos que, $(a^{(\pm)}_\mu)^\dagger = a^{*(\pm)}_\mu$, ou seja, $a^{*(\pm)}_\mu \in \mathbb{C}$. As matrizes definidas nas Eqs. (3) e (4) são matrizes coluna e linha, respectivamente

- Vamos agora definir

$$\langle \chi_\nu | V | S_{\mathbf{k_i}} \rangle \equiv c_\nu \equiv (\mathbf{c})_\nu \tag{5}$$

$$\left\langle S_{\mathbf{k_f}} \middle| V \middle| \chi_\mu \right\rangle \equiv \tilde{c}_\mu \equiv (\tilde{\mathbf{c}})_\mu \tag{6}$$

e

$$\left\langle \chi_\nu \middle| A^{(+)} \middle| \chi_\mu \right\rangle = d_{\nu\mu} \equiv (\mathbf{d})_{\nu\mu} \tag{7}$$

sendo $\mathbf{c}$ uma matriz coluna, $\tilde{\mathbf{c}}$ uma matriz linha e $\mathbf{d}$ uma matriz quadrada.

- Com a Eq. (2) na Eq. (1), temos

$$\begin{aligned}[f(\mathbf{k_f}, \mathbf{k_i})] = -\frac{1}{2\pi} \Bigg[& \sum_\mu \left\langle S_{\mathbf{k_f}} \middle| V \middle| \chi_\mu \right\rangle a_\mu^{(+)}(\mathbf{k_i}) + \sum_\nu a_\nu^{*(-)}(\mathbf{k_f}) \langle \chi_\nu | V | S_{\mathbf{k_i}} \rangle + \\ & - \sum_\mu \sum_\nu a_\nu^{*(-)}(\mathbf{k_f}) \left\langle \chi_\nu \middle| A^{(+)} \middle| \chi_\mu \right\rangle a_\mu^{(+)}(\mathbf{k_i}) \Bigg]\end{aligned} \tag{8}$$

- Substituindo (3), (4), (5), (6) e (7) na Eq. (8), obtemos

$$[f(\mathbf{k_f}, \mathbf{k_i})] = -\frac{1}{2\pi}\left[\sum_{\mu}(\tilde{\mathbf{c}})_\mu(\mathbf{a})_\mu + \sum_{\nu}(\tilde{\mathbf{a}})_\nu(\mathbf{c})_\nu - \sum_{\mu}\sum_{\nu}(\tilde{\mathbf{a}})_\nu(\mathbf{d})_{\nu\mu}(\mathbf{a})_\mu\right] \quad (9)$$

  ou ainda

$$[f(\mathbf{k_f}, \mathbf{k_i})] = -\frac{1}{2\pi}\left[\tilde{\mathbf{c}}\mathbf{a} + \tilde{\mathbf{a}}\mathbf{c} - \tilde{\mathbf{a}}\mathbf{d}\mathbf{a}\right] \quad (10)$$

- Fazendo variações de $[f(\mathbf{k_f}, \mathbf{k_i})]$ com respeito à $a_\mu^{(+)}(\mathbf{k_i})$

$$\frac{\partial[f(\mathbf{k_f}, \mathbf{k_i})]}{\partial a_\mu^{(+)}(\mathbf{k_i})} = 0$$

  considerando $a_\mu^{(+)}(\mathbf{k_i})$ [ou $(\mathbf{a})_\mu$] independente de $a_\nu^{*(-)}(\mathbf{k_f})$ [ou $(\tilde{\mathbf{a}})_\nu$], obtemos, com a equação (9):

$$\frac{\partial}{\partial(\mathbf{a})_\mu}\sum_{\mu'}(\tilde{\mathbf{c}})_{\mu'}(\mathbf{a})_{\mu'} + \cancelto{0}{\frac{\partial}{\partial(\mathbf{a})_\mu}\sum_{\nu}(\tilde{\mathbf{a}})_\nu(\mathbf{c})_\nu} - \frac{\partial}{\partial(\mathbf{a})_\mu}\sum_{\mu'}\sum_{\nu}(\tilde{\mathbf{a}})_\nu(\mathbf{d})_{\nu\mu'}(\mathbf{a})_{\mu'} = 0 \Leftrightarrow$$

$$\Leftrightarrow \sum_{\mu'}(\tilde{\mathbf{c}})_{\mu'}\delta_{\mu\mu'} - \sum_{\mu'}\sum_{\nu}(\tilde{\mathbf{a}})_\nu(\mathbf{d})_{\nu\mu'}\delta_{\mu\mu'} = 0$$

- Ou seja

$$(\tilde{\mathbf{c}})_\mu = \sum_\nu (\tilde{\mathbf{a}})_\nu (\mathbf{d})_{\nu\mu} \Rightarrow \tilde{\mathbf{c}} = \tilde{\mathbf{a}}\mathbf{d}$$

- Multiplicando a matriz inversa $\mathbf{d}^{-1}$ pela esquerda (lembrando que $\mathbf{d}\mathbf{d}^{-1} = \mathbb{1}$)

$$\tilde{\mathbf{c}}\mathbf{d}^{-1} = \tilde{\mathbf{a}}\mathbf{d}\mathbf{d}^{-1} \Rightarrow \boxed{\tilde{\mathbf{a}} = \tilde{\mathbf{c}}\mathbf{d}^{-1}} \tag{11}$$

- Com variações de $[f(\mathbf{k_f}, \mathbf{k_i})]$ com respeito à $a_\nu^{*(-)}(\mathbf{k_f})$, com $a_\nu^{*(-)}(\mathbf{k_f})$ independente de $a_\mu^{(+)}(\mathbf{k_i})$, podemos obter, com a equação (9):

$$\mathbf{c} = \mathbf{d}\mathbf{a} \Leftrightarrow \mathbf{d}^{-1}\mathbf{c} = \mathbf{d}^{-1}\mathbf{d}\mathbf{a} \Rightarrow \boxed{\mathbf{a} = \mathbf{d}^{-1}\mathbf{c}} \tag{12}$$

- Substituindo as Eqs. (11) e (12) na Eq. (10), encontramos

$$[f(\mathbf{k_f}, \mathbf{k_i})] = -\frac{1}{2\pi}\left[\tilde{\mathbf{c}}\mathbf{d}^{-1}\mathbf{c} + \tilde{\mathbf{a}}\mathbf{c} - (\tilde{\mathbf{c}}\mathbf{d}^{-1})\mathbf{d}(\mathbf{d}^{-1}\mathbf{c})\right] = -\frac{1}{2\pi}(\tilde{\mathbf{c}}\mathbf{d}^{-1}\mathbf{c}) \tag{13}$$

ou ainda, com as Eqs. (5), (6) e (7) na Eq. (13), obtemos finalmente

$$\boxed{[f(\mathbf{k_f}, \mathbf{k_i})] = -\frac{1}{2\pi}\sum_\mu \sum_\nu \left\langle S_{\mathbf{k_f}} \middle| V \middle| \chi_\mu \right\rangle (d^{-1})_{\mu\nu} \left\langle \chi_\nu \middle| V \middle| S_{\mathbf{k_i}} \right\rangle}$$

Exercício 3

- Consideremos a seguinte forma da amplitude de espalhamento

$$f(\mathbf{k_f}, \mathbf{k_i}) = -\frac{1}{2\pi} \left\langle S_{\mathbf{k_f}} \middle| V \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle \quad (14)$$

- Como $H = H_0 + V \Rightarrow V = H - H_0$, logo, em (14)

$$f(\mathbf{k_f}, \mathbf{k_i}) = -\frac{1}{2\pi} \left\langle S_{\mathbf{k_f}} \middle| (H - H_0) \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle$$

- No caso de o espalhamento de uma partícula por um potencial V, $H_0 = T_{N+1}$, com T_{N+1} sendo o operador energia cinética da partícula incidente
- O elemento de matriz envolvendo T_{N+1} é dado por:

$$\left\langle S_{\mathbf{k_f}} \middle| T_{N+1} \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle = -\frac{1}{2} \int d^3 r S^*_{\mathbf{k_f}} \nabla^2_{N+1} \Psi^{(+)}_{\mathbf{k_i}} \quad (15)$$

com $S_{\mathbf{k_f}} = S_{\mathbf{k_f}}(\mathbf{r_1}, ..., \mathbf{r_{N+1}})$ e $\Psi^{(+)}_{\mathbf{k_i}} = \Psi^{(+)}_{\mathbf{k_i}}(\mathbf{r_1}, ..., \mathbf{r_{N+1}})$

- Para simplificar nosso raciocínio, consideremos o caso 1D da equação (15)
- Integrando por partes, temos:

$$\frac{1}{2}\int dx S^*_{\mathbf{k_f}} \frac{d^2}{dx^2}\Psi^{(+)}_{\mathbf{k_i}} = \frac{1}{2}\left[S^*_{\mathbf{k_f}} \frac{d\Psi^{(+)}_{\mathbf{k_i}}}{dx}\Bigg|_{-\infty}^{+\infty} - \frac{dS^*_{\mathbf{k_f}}}{dx}\Psi^{(+)}_{\mathbf{k_i}}\Bigg|_{-\infty}^{+\infty} + \int dx \Psi^{(+)}_{\mathbf{k_i}} \frac{d^2 S^*_{\mathbf{k_f}}}{dx^2}\right]$$

- No geral, $S_{\mathbf{k_f}}$ e $\frac{dS_{\mathbf{k_f}}}{dx}$ (ou ainda, $\nabla_{\mathbf{N+1}} S_{\mathbf{k_f}}$) não se anulam no infinito
- Para termos

$$f(\mathbf{k_f}, \mathbf{k_i}) = -\frac{1}{2\pi}\left\langle S_{\mathbf{k_f}} \middle| (H - H_0) \middle| \Psi^{(+)}_{\mathbf{k_i}} \right\rangle = 0$$

$\Psi^{(+)}_{\mathbf{k_i}}$ e $\nabla_{\mathbf{N+1}}\Psi^{(+)}_{\mathbf{k_i}}$ devem se anular para obtermos os elementos de matriz nulos envolvendo T_{N+1} e assim garantir que T_{N+1} seja hermitiano para elementos de matriz envolvendo funções quadraticamente integráveis