Mott problem

For a system of two hydrogen atoms and an α particle the hamiltonian is

$$\hat{H} = \hat{K}_\alpha + \hat{K}_1 + \hat{K}_2 + V_1 + V_2 + U_1 + U_2$$

where

$$\hat{K}_\alpha = -\frac{\hbar^2}{2M}\nabla_\alpha^2 \qquad \text{kinetic energy of } \alpha \text{ particle}$$

$$\hat{K}_1 = -\frac{\hbar^2}{2m}\nabla_1^2 \qquad \text{kinetic energy of 1st electron}$$

$$\hat{K}_2 = -\frac{\hbar^2}{2m}\nabla_2^2 \qquad \text{kinetic energy of 2nd electron}$$

$$V_1 = -\frac{e^2}{|\mathbf{r}_1 - \mathbf{a}_1|} \qquad \text{potential energy of 1st electron}$$

$$V_2 = -\frac{e^2}{|\mathbf{r}_2 - \mathbf{a}_2|} \qquad \text{potential energy of 2nd electron}$$

$$U_1 = -\frac{2e^2}{|\mathbf{R} - \mathbf{r}_1|} \qquad \text{potential energy of } \alpha \text{ and 1st electron}$$

$$U_2 = -\frac{2e^2}{|\mathbf{R} - \mathbf{r}_2|} \qquad \text{potential energy of } \alpha \text{ and 2nd electron}$$

and

$$\mathbf{R} \qquad \text{coordinate of } \alpha \text{ particle}$$
$$\mathbf{r}_1, \mathbf{r}_2 \qquad \text{coordinates of electrons}$$
$$\mathbf{a}_1, \mathbf{a}_2 \qquad \text{coordinates of hydrogen atoms}$$

Let ψ_1 and ψ_2 be hydrogen atom wavefunctions such that

$$\hat{H}\psi_1 = E_1\psi_1, \quad \hat{H}\psi_2 = E_2\psi_2$$

We want to find a wavefunction $F(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2)$ such that

$$\hat{H}F = EF$$

Let

$$F = F_0 + F_1 + F_2 + \cdots$$

and let

$$\hat{H}_0 = \hat{K}_\alpha + E_1 + E_2$$

Start by finding an F_0 such that

$$\hat{H}_0 F_0 = EF_0$$

The solution is
$$F_0(\mathbf{R}, \mathbf{r}_1, \mathbf{r}_2) = f_0(\mathbf{R})\psi_1(\mathbf{r}_1 - \mathbf{a}_1)\psi_2(\mathbf{r}_2 - \mathbf{a}_2) \tag{1}$$

where
$$f_0(\mathbf{R}) = \frac{1}{|\mathbf{R}|}\exp\left(\frac{ik|\mathbf{R}|}{\hbar}\right), \quad k = \sqrt{2M(E - E_1 - E_2)}$$

It follows that for the full hamiltonian
$$\hat{H}F_0 = EF_0 + (U_1 + U_2)F_0$$

To cancel $(U_1 + U_2)F_0$ from the full hamiltonian, find an F_1 such that
$$\hat{H}_0 F_1 = EF_1 - (U_1 + U_2)F_0$$

Rewrite as
$$\left(\hat{H}_0 - E\right)F_1 = -(U_1 + U_2)F_0$$

Expand F_1 and F_0.
$$\left(\hat{H}_0 - E\right)f_1(\mathbf{R})\psi_1(\mathbf{r}_1 - \mathbf{a}_1)\psi_2(\mathbf{r}_2 - \mathbf{a}_2) = -(U_1 + U_2)f_0(\mathbf{R})\psi_1(\mathbf{r}_1 - \mathbf{a}_1)\psi_2(\mathbf{r}_2 - \mathbf{a}_2)$$

To solve for $f_1(\mathbf{R})$ multiply both sides by
$$\psi_1^*(\mathbf{r}_1 - \mathbf{a}_1)\psi_2^*(\mathbf{r}_2 - \mathbf{a}_2)$$

and integrate over $\mathbf{r}_1$ and $\mathbf{r}_2$ to obtain
$$\left(\hat{H}_0 - E\right)f_1(\mathbf{R}) = V(\mathbf{R})f_0(\mathbf{R}) \tag{2}$$

where
$$V(\mathbf{R}) = 2e^2 \int \frac{|\psi_1(\mathbf{r}_1 - \mathbf{a}_1)|^2 \, |\psi_2(\mathbf{r}_2 - \mathbf{a}_2)|^2}{|\mathbf{R} - \mathbf{r}_1|} \, d\mathbf{r}_1 \, d\mathbf{r}_2$$
$$+ 2e^2 \int \frac{|\psi_1(\mathbf{r}_1 - \mathbf{a}_1)|^2 \, |\psi_2(\mathbf{r}_2 - \mathbf{a}_2)|^2}{|\mathbf{R} - \mathbf{r}_2|} \, d\mathbf{r}_1 \, d\mathbf{r}_2$$

Because $|\psi|^2$ is a probability density function we have
$$V(\mathbf{R}) = 2e^2 \int \frac{|\psi_1(\mathbf{r}_1 - \mathbf{a}_1)|^2}{|\mathbf{R} - \mathbf{r}_1|} \, d\mathbf{r}_1 + 2e^2 \int \frac{|\psi_2(\mathbf{r}_2 - \mathbf{a}_2)|^2}{|\mathbf{R} - \mathbf{r}_2|} \, d\mathbf{r}_2$$

Per Mott the solution to (2) is
$$f_1(\mathbf{R}) = \frac{M}{2\pi\hbar^2} \int \frac{V(\mathbf{r})f_0(\mathbf{r})}{|\mathbf{R} - \mathbf{r}|} \exp\left(\frac{ik|\mathbf{R} - \mathbf{r}|}{\hbar}\right) d\mathbf{r}, \quad k = \sqrt{2M(E - E_1 - E_2)}$$

Substitute for $f_0(\mathbf{r})$ to obtain
$$f_1(\mathbf{R}) = \frac{M}{2\pi\hbar^2} \int \frac{V(\mathbf{r})}{|\mathbf{R} - \mathbf{r}||\mathbf{r}|} \exp\left(\frac{ik|\mathbf{R} - \mathbf{r}|}{\hbar} + \frac{ik|\mathbf{r}|}{\hbar}\right) d\mathbf{r}$$

Change of variable $\mathbf{r} \to \mathbf{y} + \mathbf{a}_1$.

$$f_1(\mathbf{R}) = \frac{M}{2\pi\hbar^2} \int \frac{V(\mathbf{y} + \mathbf{a}_1)}{|\mathbf{R} - \mathbf{y} - \mathbf{a}_1||\mathbf{y} + \mathbf{a}_1|} \exp\left(\frac{ik|\mathbf{R} - \mathbf{y} - \mathbf{a}_1|}{\hbar} + \frac{ik|\mathbf{y} + \mathbf{a}_1|}{\hbar}\right) d\mathbf{y}$$

Per Mott (see also Figari and Teta)

$$f_1(\mathbf{R}) \approx \frac{\exp(ik|\mathbf{R} - \mathbf{a}_1|)}{|\mathbf{R} - \mathbf{a}_1|} \frac{M}{2\pi\hbar^2} \int \frac{V(\mathbf{y} + \mathbf{a}_1)}{|\mathbf{y} + \mathbf{a}_1|} \exp\left(-\frac{ik\mathbf{u} \cdot \mathbf{y}}{\hbar} + \frac{ik|\mathbf{y}|}{\hbar}\right) d\mathbf{y} \qquad (3)$$

where

$$\mathbf{u} = \frac{\mathbf{R} - \mathbf{a}_1}{|\mathbf{R} - \mathbf{a}_1|}$$

By the method of stationary phase the integral vanishes except for

$$\frac{d}{d\mathbf{y}}\left(-\mathbf{u} \cdot \mathbf{y} + |\mathbf{y} + \mathbf{a}_1|\right) = -\mathbf{u} + \frac{\mathbf{y} + \mathbf{a}_1}{|\mathbf{y} + \mathbf{a}_1|} = 0$$

The $V(\mathbf{y} + \mathbf{a}_1)$ in (3) shrinks as $\mathbf{y}$ grows hence for $\mathbf{y} \ll \mathbf{a}_1$ we have the approximation

$$\mathbf{u} \approx \frac{\mathbf{a}_1}{|\mathbf{a}_1|}$$

Hence the α particle trajectory is along the line $\mathbf{a}_1$.