Spontaneous decay of resonant energy levels for molecules with moving nuclei

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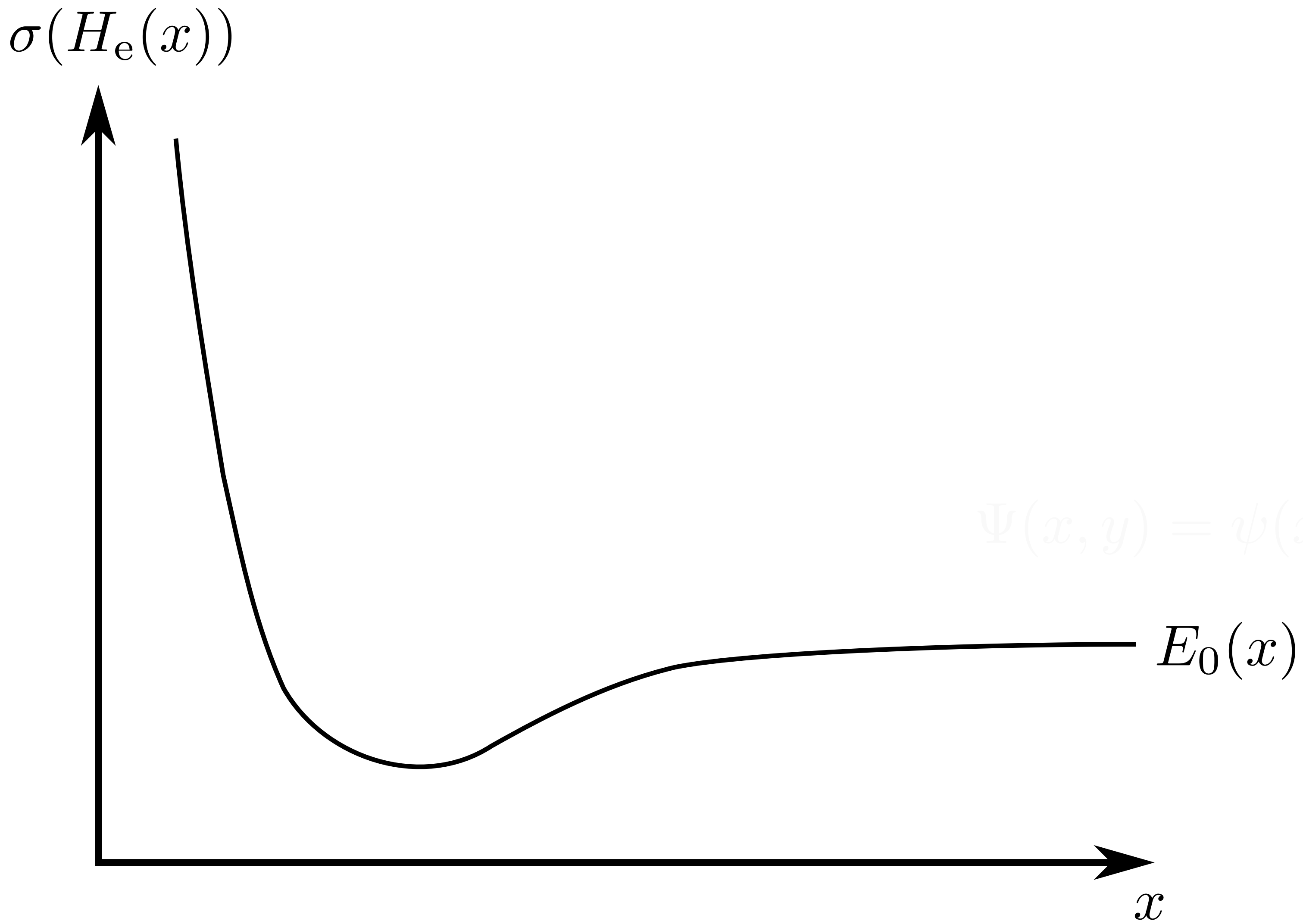
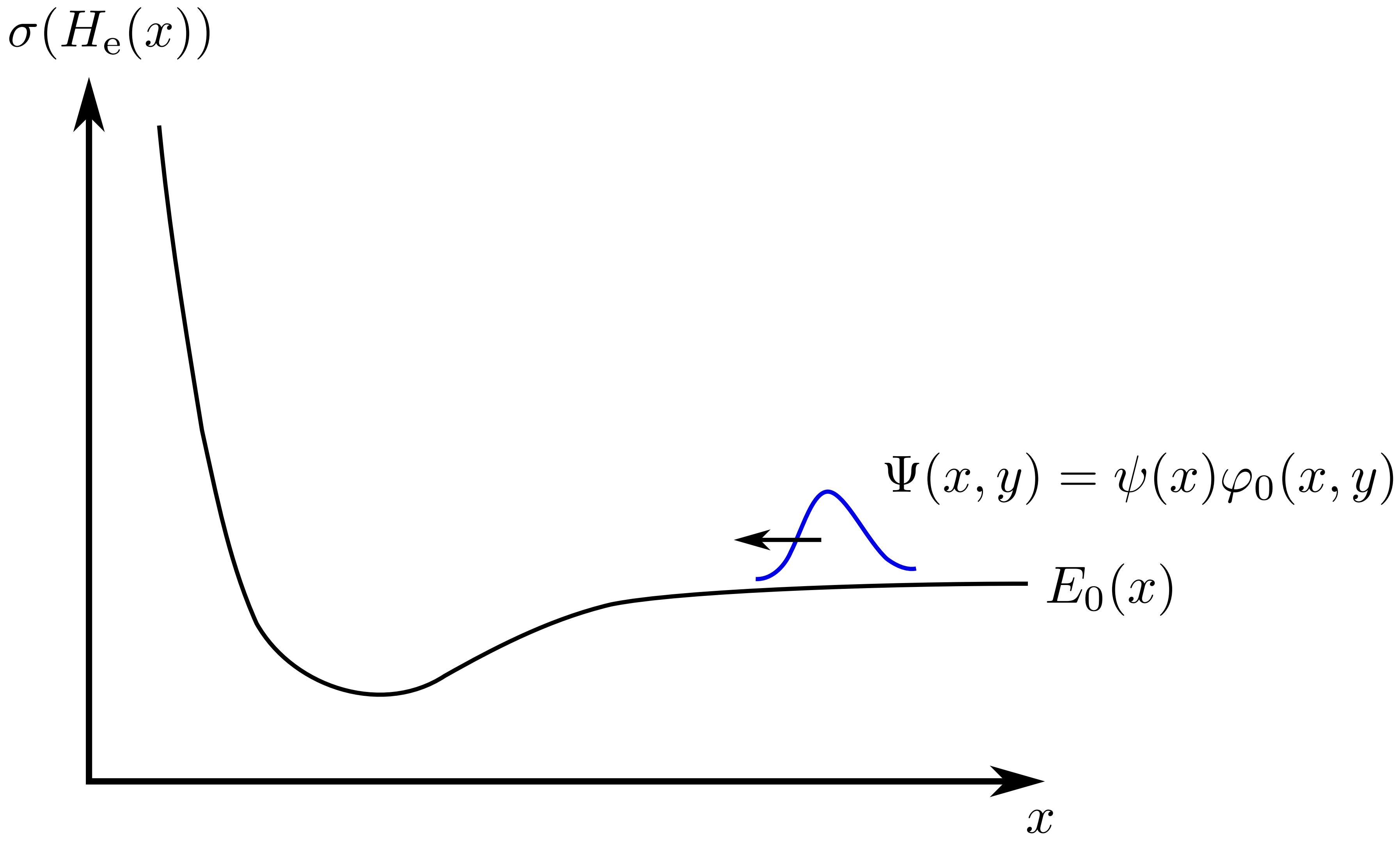
Jointly with Jakob Wachsmuth


$\sigma(H_{\mathrm{e}}(x))$
$\Psi(x,y) = \psi(x)\varphi_0(x,y)$
$E_0(x)$
x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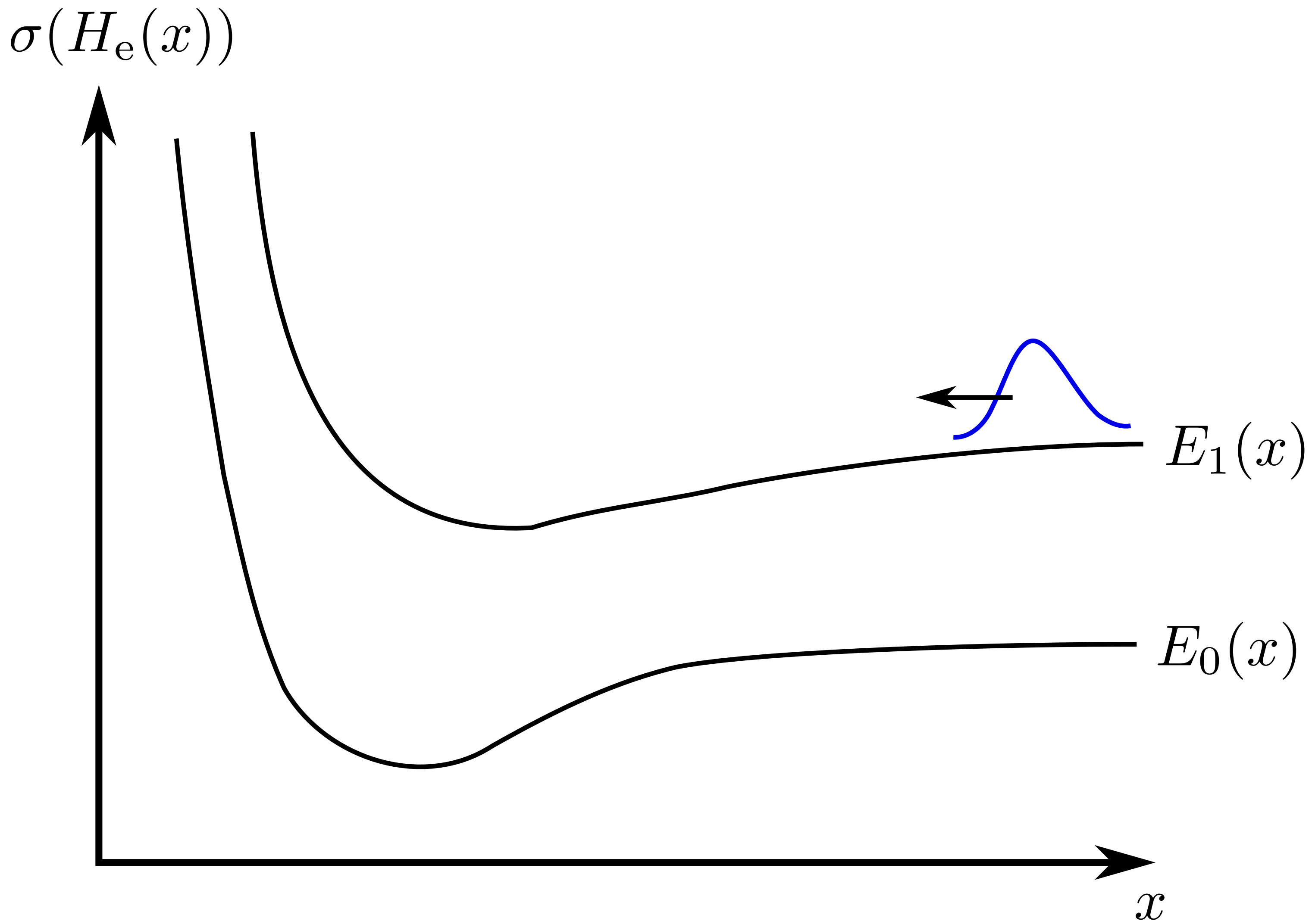
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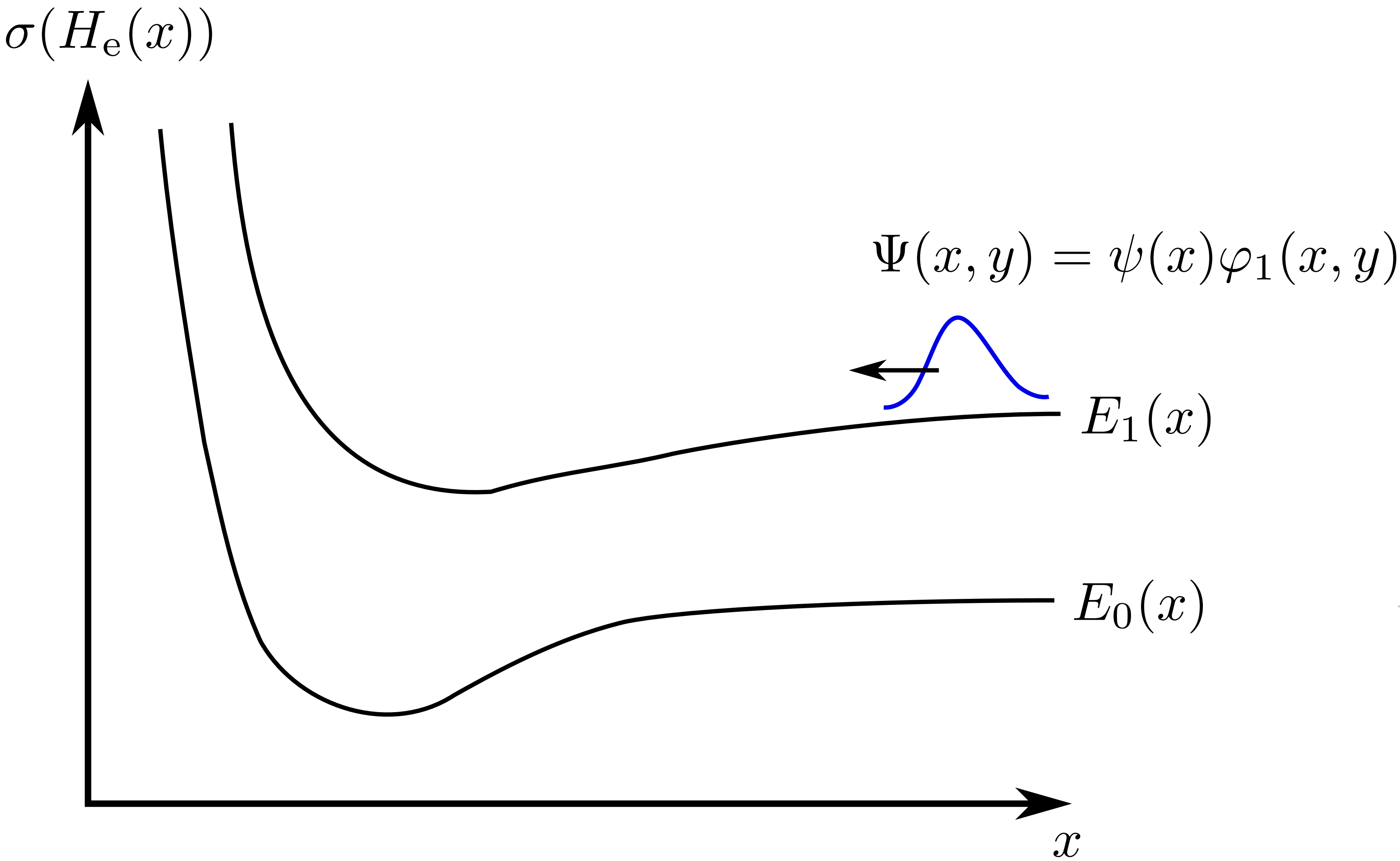

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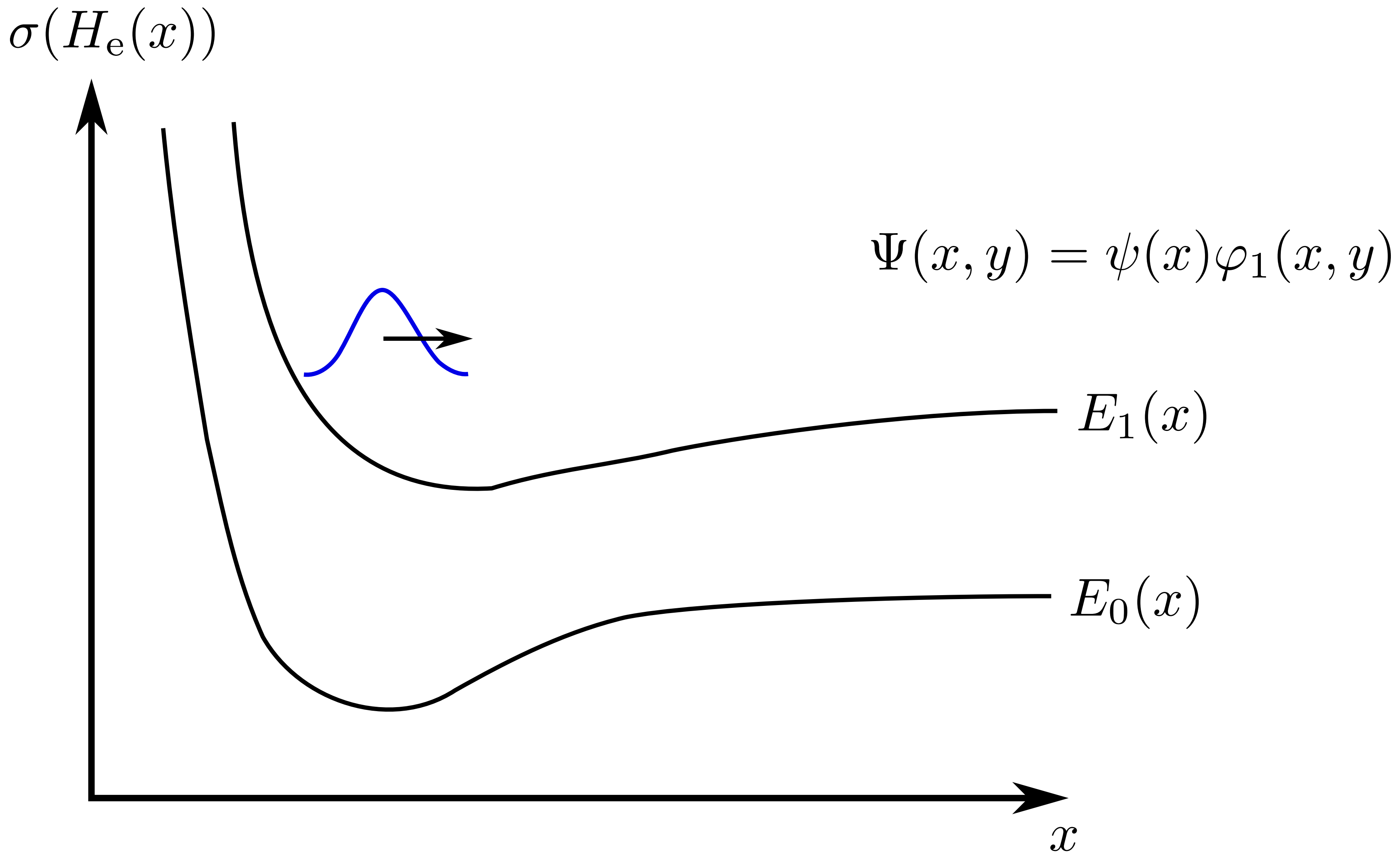
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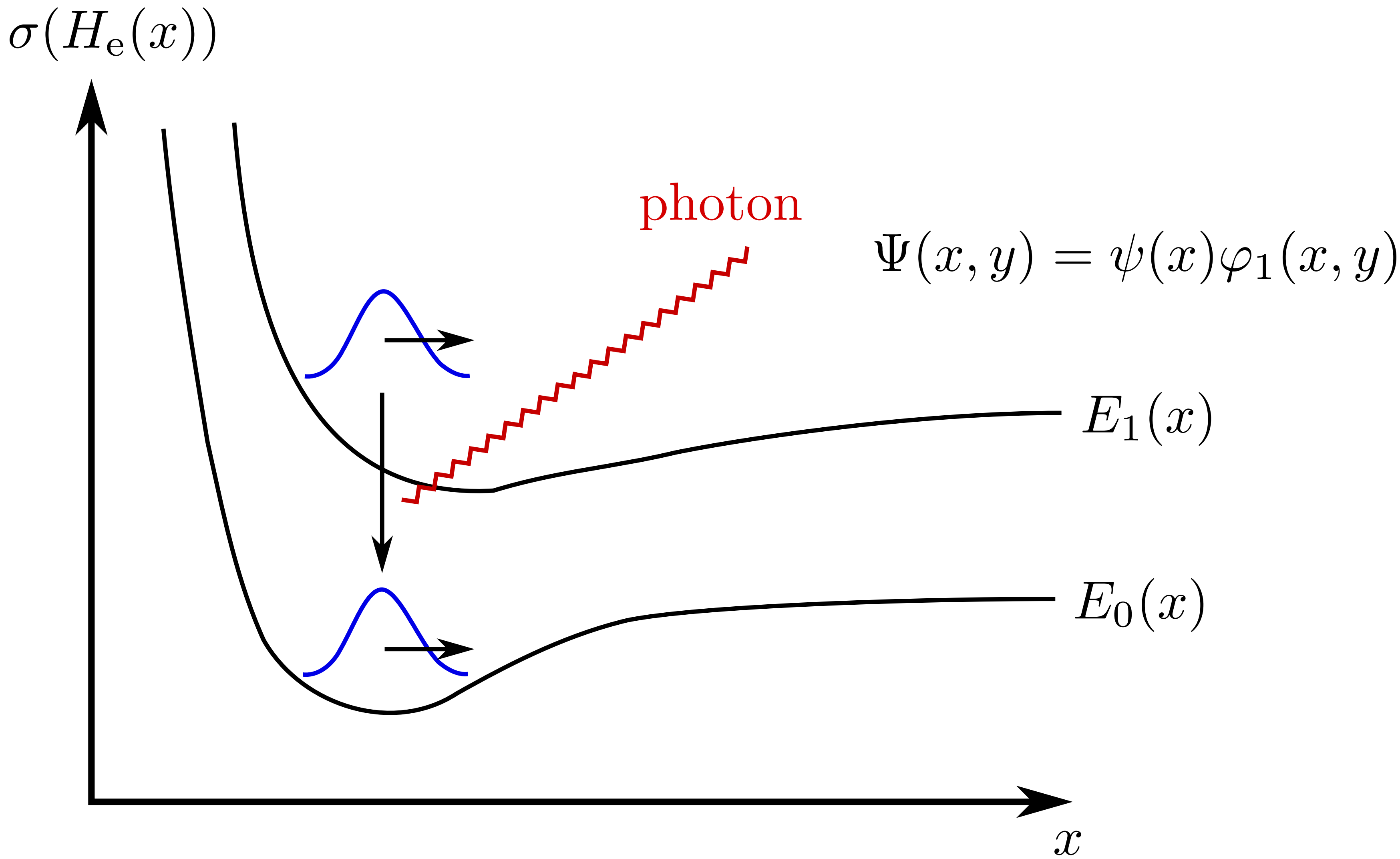
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photon
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$E_1(x)$
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Unit of energy: Rydberg $= 2m\alpha^2$

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$$H = \frac{m}{M} \sum_{j=1}^{N_{\mathsf{n}}} \left(p_{j,x} - 2\sqrt{\pi}\alpha^{\frac{3}{2}} Z_j \, A_\lambda(\alpha x_j) \right)^2 \qquad \text{nuclei}$$

$$+ \sum_{j=1}^{N_{\mathsf{e}}} \left(p_{j,y} - 2\sqrt{\pi}\alpha^{\frac{3}{2}} \, A_\lambda(\alpha y_j) \right)^2 \qquad \text{electrons}$$

$$+ H_{\mathsf{f}} \qquad \text{photons}$$

$$+ V_{\mathsf{e}}(y) + V_{\mathsf{en}}(x,y) + V_{\mathsf{n}}(x) \qquad \text{electrostatic interactions}$$

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The Born-Oppenheimer approximation is good when $\varepsilon := \sqrt{\frac{m}{M}} \ll 1$.

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$\Rightarrow$ two small parameters, ε and α.

2.1. Dynamical molecules without field ($\varepsilon > 0$, $\alpha = 0$)

Let

$$H_{\mathsf{mol}} := -\varepsilon^2 \sum_{j=1}^{N_{\mathsf{n}}} \Delta_{x_j} + H_{\mathsf{e}}(x)$$

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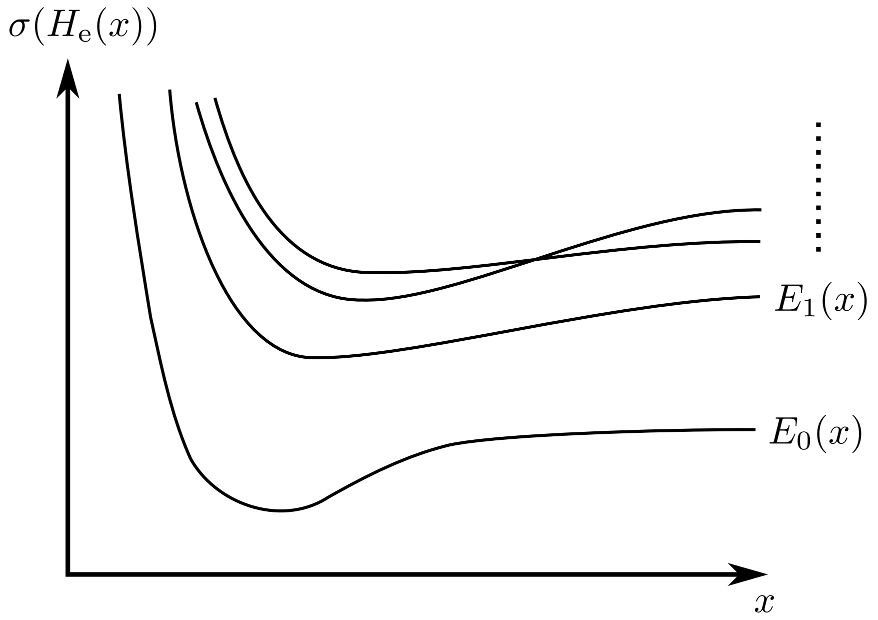
Electronic energy surfaces:

Use pointwise eigenprojections

$$H_{\mathrm{e}}(x)P_j(x) = E_j(x)P_j(x)$$

to define projection on the full space

$$(P_j\Psi)(x,y) := P_j(x)\Psi(x,y)\,.$$



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$$H_{j,\mathrm{diag}} := P_j H_{\mathrm{mol}} P_j \;+\; (1 - P_j) H_{\mathrm{mol}} (1 - P_j)$$

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Typical Result 1 (Time-dependent Born-Oppenheimer)
(c.f. Spohn-T. '01, Martinez-Sordoni '02, '09)

Assume a gap condition. Then for any $E < \infty$

$$\left\| \left(\mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon} H_{\mathrm{mol}}} - \mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon} H_{j,\mathrm{diag}}} \right) \mathbf{1}_{(-\infty,E]}(H_{\mathrm{mol}}) \right\| \leq C_E \, \varepsilon \, |t| \, .$$

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Since

$$H_{j,\text{od}} := (1 - P_j) \, H_{\text{mol}} \, P_j + P_j \, H_{\text{mol}} \, (1 - P_j) = \mathcal{O}(\varepsilon)$$

but not smaller, this does not follow just from time-dependent perturbation theory,

$$\mathrm{e}^{-\mathrm{i} H_{\text{mol}} \frac{t}{\varepsilon}} \approx \mathrm{e}^{-\mathrm{i} H_{j,\text{diag}} \frac{t}{\varepsilon}} - \frac{\mathrm{i}}{\varepsilon} \int_0^t \mathrm{e}^{\mathrm{i} H_{j,\text{diag}} \frac{s-t}{\varepsilon}} \, H_{j,\text{od}} \, \mathrm{e}^{-\mathrm{i} H_{j,\text{diag}} \frac{s}{\varepsilon}} \, \mathrm{d}s$$

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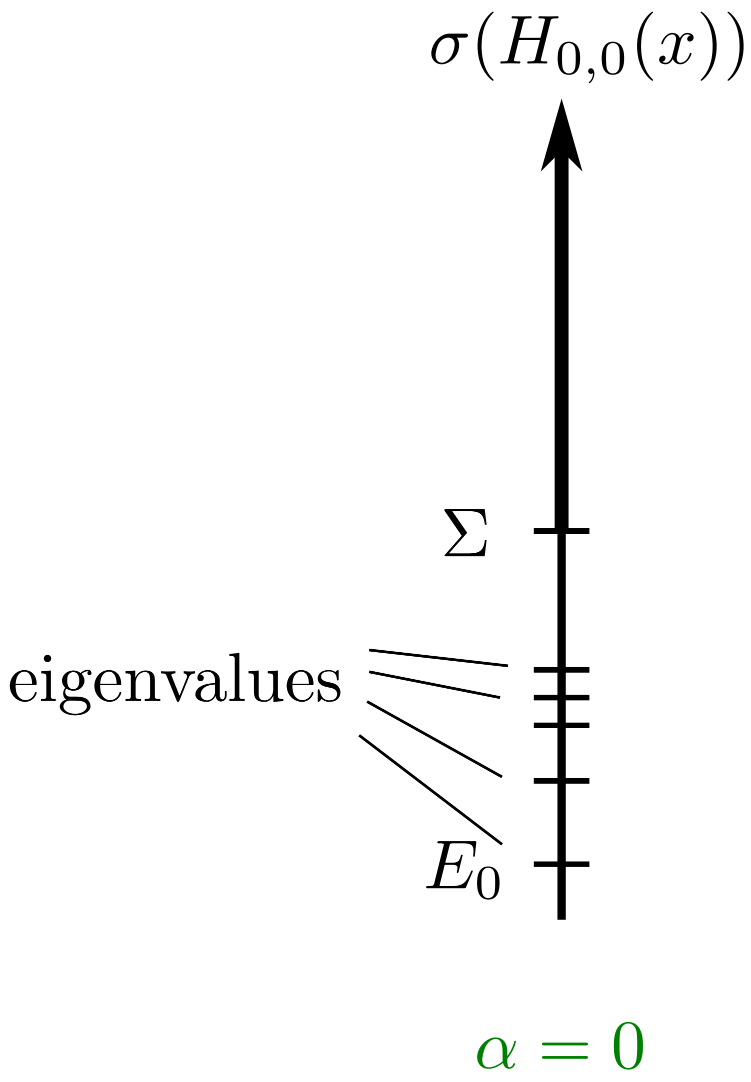
On $\Psi(x,y) = \psi(x)\varphi_j(x,y) \in P_j \mathcal{H}_{\mathrm{mol}}$ the diagonal Hamiltonian acts as

$$(H_{j,\mathrm{diag}} \Psi)(x,y) =: (H_{j,\mathrm{BO}} \psi)(x) \varphi_j(x,y)$$

with

$$H_{j,\mathrm{BO}} = \varepsilon^2 (-\mathrm{i}\nabla_x - A_{\mathrm{Berry}}(x))^2 + E_j(x) + \mathcal{O}(\varepsilon^2) \, .$$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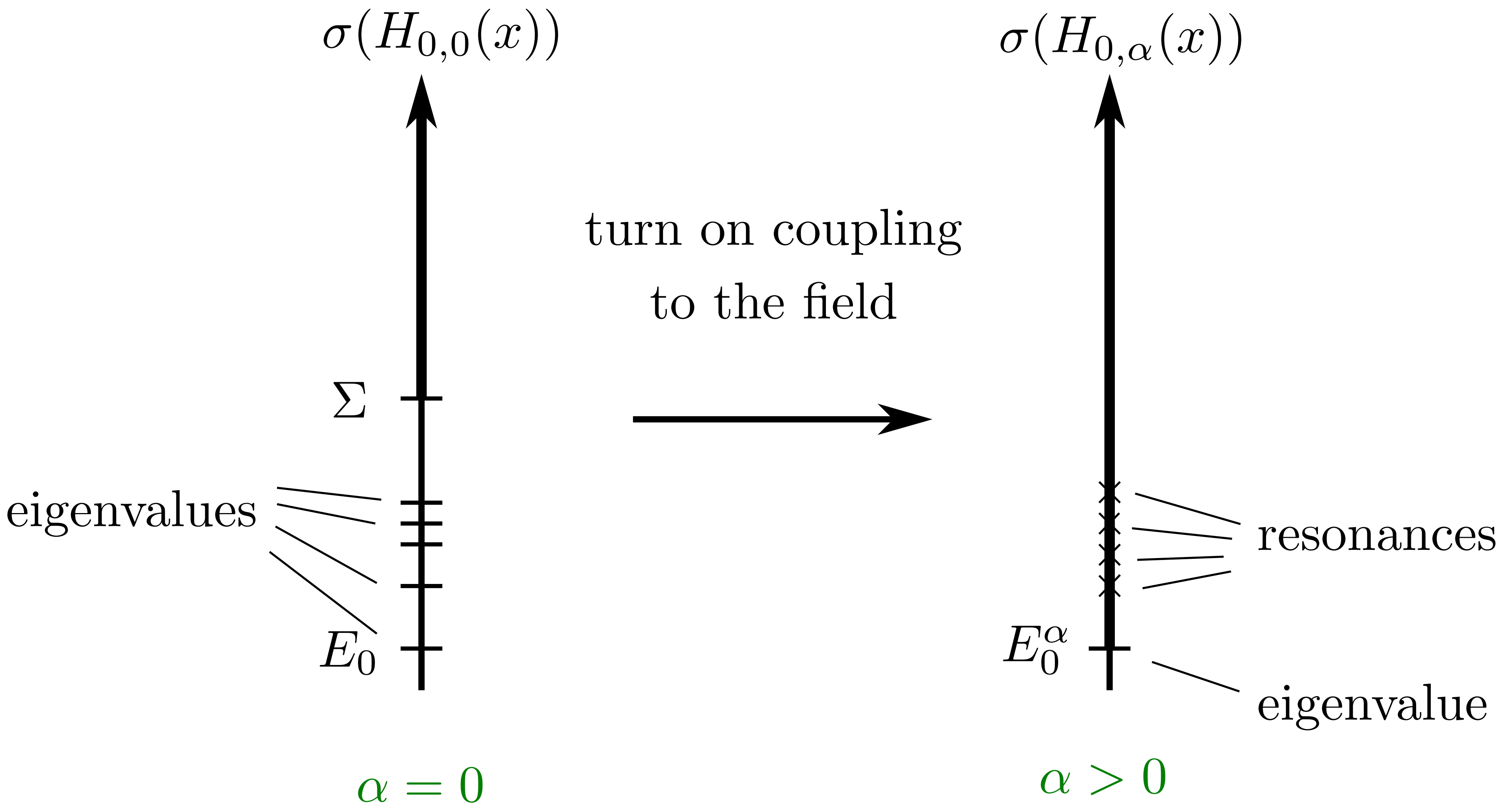
$\sigma(H_{0,0}(x))$
Σ
eigenvalues
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turn on coupling
to the field
$\sigma(H_{0,\alpha}(x))$
resonances
E_0^α
eigenvalue
$\alpha > 0$

Typical Result 2 (Decay of resonances)

(c.f. Bach-Fröhlich-Sigal '99, Hasler-Herbst-Huber '07, Abou Salem-Faupin-Fröhlich-Sigal '08, Faupin '08)

Let $\Psi_j = \varphi_j \otimes \Omega$, *then*

$$\left|\left\langle \Psi_j, \mathrm{e}^{-\mathrm{i}tH_{0,\alpha}} \Psi_j \right\rangle\right| = \mathrm{e}^{-t\alpha^3\gamma_j} + \mathcal{O}(\alpha^{\frac{1}{2}})$$

with $\gamma_j > 0$.

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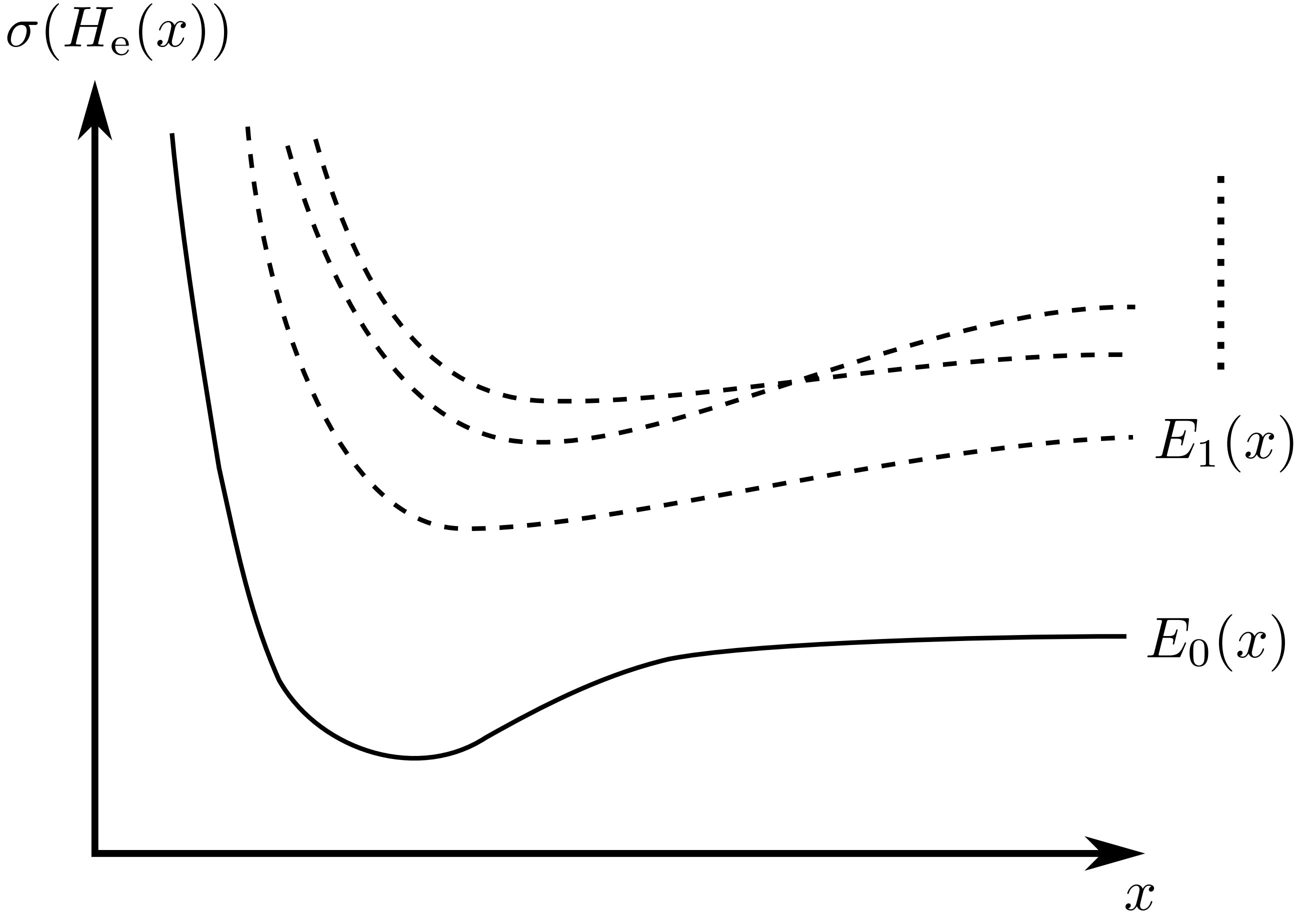
$$\Rightarrow \qquad \text{lifetime} \sim \frac{1}{\alpha^3}$$

The excited electronic levels turn into resonances.



2.3. Dynamical molecules coupled to the field ($\varepsilon > 0$, $\alpha > 0$)

Goal #1: Show that the BO-approximation is still valid, because

$$\text{lifetime } \sim \alpha^{-3} \quad \gg \quad \text{time-scale of molecular dynamics } \sim \varepsilon^{-1}$$

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Check: $m_{\mathrm{p}} \leq M \leq 250 m_{\mathrm{p}} \quad \Rightarrow \quad \varepsilon_{\min} := \frac{1}{680} \leq \varepsilon \leq \frac{1}{43} =: \varepsilon_{\max}$

Since $(137)^3 \gg 680$ this assumption is typically satisfied.

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To keep better track of the relative size of errors we couple the two small parameters and put

$$\alpha = \varepsilon^{\beta} \quad \text{with} \quad \beta_{\mathrm{min}} = \frac{\ln \alpha}{\ln \varepsilon_{\mathrm{min}}} \approx 0,75\,, \quad \beta_{\mathrm{max}} = \frac{\ln \alpha}{\ln \varepsilon_{\mathrm{max}}} \approx 1,3\,.$$

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Our results hold for $\frac{5}{6} < \beta < \frac{3}{2}$, corresponding to $m_\mathrm{p} \le M \le 72 m_\mathrm{p}$.

Goal #1: Show that the BO-approximation is still valid, because

$$\text{lifetime } \sim \alpha^{-3} \quad \gg \quad \text{time-scale of molecular dynamics } \sim \varepsilon^{-1}$$

Goal #2: Quantify spontaneous emission at leading order.

Expectation: probability for spontaneous emission $\sim \alpha^3 \frac{t}{\varepsilon} = \varepsilon^{3\beta-1} t$.

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\begin{aligned}
H^\varepsilon \;=\; & -\varepsilon^2 \sum_{j=1}^{N_\mathsf{n}} \Delta_{x_j} + H_\mathsf{e}(x) + H_\mathsf{f} && \mathcal{O}(1) \\
& -\varepsilon^{\frac{3}{2}\beta} 4\sqrt{\pi} \sum_{j=1}^{N_\mathsf{e}} A_\lambda(\varepsilon^\beta y_j) \cdot p_{j,y} && \mathcal{O}(\varepsilon^{\frac{3}{2}\beta}) \\
& + \mathcal{O}(\varepsilon^{\frac{3}{2}\beta+1})
\end{aligned}
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$\Rightarrow$ Goal #1 can be achieved by standard time-dep. perturbation theory

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Problem #1: $\|\text{BO-error}\| \sim \varepsilon$ and $\|\text{Effect}\| \sim \varepsilon^{\frac{3}{2}\beta-\frac{1}{2}}$

$\Rightarrow$ Effect $\leq$ Error for $\beta \geq 1$.

Goal #2: Quantify spontaneous emission at leading order.

Expectation: probability for spontaneous emission $\sim \alpha^3 \frac{t}{\varepsilon} = \varepsilon^{3\beta-1} t$.

$$H^\varepsilon = -\varepsilon^2 \sum_{j=1}^{N_\mathsf{n}} \Delta_{x_j} + H_\mathsf{e}(x) + H_\mathsf{f} \qquad \mathcal{O}(1)$$

$$- \varepsilon^{\frac{3}{2}\beta} 4\sqrt{\pi} \sum_{j=1}^{N_\mathsf{e}} A_\lambda(\varepsilon^\beta y_j) \cdot p_{j,y} \qquad \mathcal{O}(\varepsilon^{\frac{3}{2}\beta})$$

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Problem #1: $\|\text{BO-error}\| \sim \varepsilon$ and $\|\text{Effect}\| \sim \varepsilon^{\frac{3}{2}\beta-\frac{1}{2}}$

$\Rightarrow$ Effect $\leq$ Error for $\beta \geq 1$.

Solution: Improved BO-approximation using super-adiabatic subspaces P_j^ε

Goal #2: Quantify spontaneous emission at leading order.

Expectation: probability for spontaneous emission $\sim \alpha^3 \frac{t}{\varepsilon} = \varepsilon^{3\beta-1} t$.

$$H^\varepsilon = -\varepsilon^2 \sum_{j=1}^{N_n} \Delta_{x_j} + H_e(x) + H_f \qquad \mathcal{O}(1)$$

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$$+ \mathcal{O}(\varepsilon^{\frac{3}{2}\beta+1})$$

Problem #2: The effect is smaller than expected from naive perturbation theory, which would be $\sim (\varepsilon^{\frac{3}{2}\beta-1})^2 = \varepsilon^{3\beta-2}$

$$e^{-iH^\varepsilon \frac{t}{\varepsilon}} \approx e^{-iH_0 \frac{t}{\varepsilon}} - i\frac{\varepsilon^{\frac{3}{2}\beta}}{\varepsilon} \int_0^t e^{iH_0 \frac{s-t}{\varepsilon}} H_1 e^{-iH_0 \frac{s}{\varepsilon}} ds$$

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Solution: "Dressed" super-adiabatic subspaces $P^{\varepsilon,\delta}_{j,\mathsf{vac}}$ with

$$[P^{\varepsilon,\delta}_{j,\mathsf{vac}}, H^\varepsilon] = \mathcal{O}(\varepsilon^{\frac{3}{2}\beta}\delta^{\frac{1}{2}})$$

Theorem 1 (BO without field)

Let $E < \infty$ *and* $\chi_E = \mathbf{1}_{(-\infty,E]}$. *For each isolated energy surface* E_j *there exists an orthogonal projection* P_j^ε *such that*

$$\|P_j^\varepsilon - P_j\|_{\mathcal{L}(D^n)} \leq C_n \, \varepsilon$$

and

$$\left\| \left[H_{\mathrm{mol}}^\varepsilon, P_j^\varepsilon \right] \chi_E(H_{\mathrm{mol}}^\varepsilon) \right\|_{\mathcal{L}(\mathcal{H},D^n)} \leq C_n \, \varepsilon^3 \, .$$

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$$\left\|\left[H^\varepsilon_{\mathsf{mol}}, P_j^\varepsilon\right]\chi_E(H^\varepsilon_{\mathsf{mol}})\right\|_{\mathcal{L}(\mathcal{H},D^n)} \leq C_n\,\varepsilon^3\,.$$

As a consequence one has for

$$H^\varepsilon_{j,\mathsf{diag}} := P_j^\varepsilon H^\varepsilon_{\mathsf{mol}} P_j^\varepsilon + (1 - P_j^\varepsilon) H^\varepsilon_{\mathsf{mol}} (1 - P_j^\varepsilon)$$

that

$$\left\|\left(\mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon}H^\varepsilon_{\mathsf{mol}}} - \mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon}H^\varepsilon_{j,\mathsf{diag}}}\right)\chi_E(H^\varepsilon_{\mathsf{mol}})\right\|_{\mathcal{L}(\mathcal{H},D)} \leq C_E\,\varepsilon^2|t|\,.$$

Corollary 1 (BO with field)

Under the same assumptions we have that

$$\left\| \left(\mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon}H^\varepsilon} - \mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon}(H^\varepsilon_{j,\mathrm{diag}} \otimes \mathbf{1} + \mathbf{1} \otimes H_\mathrm{f})} \right) \chi_E(H^\varepsilon) \right\|_{\mathcal{L}(\mathcal{H})} \leq C_E\, \varepsilon^{\frac{3}{2}\beta - 1} |t| \,.$$

Theorem 2 (spontaneous emission: probability)

Let $\Psi = \psi \otimes \Omega \in (P_j^\varepsilon \otimes P_\Omega)\, \chi_E(H^\varepsilon)\mathcal{H}$ *, then*

$$\left\| P_i^\varepsilon \, \mathrm{e}^{-\mathrm{i}\frac{t}{\varepsilon}H^\varepsilon} \, \Psi \right\|^2 \;=\; \frac{4\alpha^3}{3}\frac{1}{\varepsilon}\int_0^t \mathrm{d}s \, \left\langle \psi(s), \, |D_{ij}|^2 \Delta_E^3 \, \psi(s) \right\rangle_{\mathcal{H}_{\mathrm{nuc}}} \, + \, o(\varepsilon^{3\beta-1})$$

uniformly on bounded intervals in time.

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uniformly on bounded intervals in time.

Here

$$\psi(s) := \mathrm{e}^{-\mathrm{i}\frac{s}{\varepsilon}H_{j,\mathrm{BO}}} \, P_j \, \psi$$

is the nuclear wave function according to the standard BO-approximation,

$$D_{ij}(x) = \sum_{\ell=1}^{N_{\mathrm{e}}} \langle \varphi_i(x), y_\ell \varphi_j(x) \rangle_{\mathcal{H}_{\mathrm{el}}}$$

is the dipole matrix element and $\Delta_E(x) = E_j(x) - E_i(x)$ the energy gap.

- S.T., Jakob Wachsmuth, *Commun. Math. Phys.* **315** (2012), 699–738.

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Thank you for listening !