FYS4480 Oral exam, midterm one and two

Helium and Beryllium using CIS and Hartree-Fock, pairing model

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SETUP

Represent states using creation $a_p^\dagger$ and annihilation a_q operators (occupation representation/second quantization), obeying

$$\{a_p^\dagger, a_q\} = \delta_{pq}, \qquad \{a_p^\dagger, a_q^\dagger\} = \{a_p, a_q\} = 0$$

p and q are sets of relevant quantum numbers. We need to pick a single particle (SP) computational basis, having n possible single particle states.

$$\text{3D HO:} \qquad p = \{n_r, l, m_l, s, m_s\}, \qquad a_p^\dagger |0\rangle = |p\rangle \longrightarrow \psi_p(\mathbf{x}) = \psi_{n_r lm}(r, \theta, \phi) = \ldots$$

Need a Hamiltonian to solve $\hat{H} = \hat{H}_0 + \hat{V}$, with $\hat{H}_0$ representing single particle energy contributions, and $\hat{V}$ interactions.

Often start with an N-particle ground state ansatz $|\Phi_0\rangle = a_1^\dagger, \ldots a_N^\dagger |0\rangle$.

And consider excitations of this

$$\begin{aligned} \text{1p1h} \qquad & |\Phi_i^a\rangle = a_a^\dagger a_i |\Phi_0\rangle \\ \text{2p2h} \qquad & |\Phi_{ij}^{ab}\rangle = a_a^\dagger a_b^\dagger a_j a_i |\Phi_0\rangle \\ \text{NpNh} \qquad & |\Phi_{ij\ldots}^{ab\ldots}\rangle = a_a^\dagger a_b^\dagger \ldots a_j a_i |\Phi_0\rangle \end{aligned}$$

Full configuration interaction (FCI)

Start with N particle ground state ansatz $|\Phi_0\rangle$.

Not an eigenstate of $\hat{V}$ and therefor not the true ground state of the system.

By considering every possible N particle state in our system (using $\{a_1^\dagger, \ldots, a_N^\dagger, \ldots, a_n^\dagger\}$), we can construct our ground state $|\Psi_0\rangle$ as a linear combination of excited states.

$$|\Psi_0\rangle = C_0 |\Phi_0\rangle + \sum_{ai} C_i^a |\Phi_i^a\rangle + \sum_{abij} C_{ij}^{ab} |\Phi_{ij}^{ab}\rangle + \ldots$$

Normally solved by considering the Hamiltonian in matrix representation, with elements $H_{XY} = \langle\Phi_X| \hat{H} |\Phi_Y\rangle$, with $X, Y \in \{\text{0p0h}, \text{1p1h} \ldots \text{NpNh}\}$, giving the eigenvalue problem

$$H\mathbf{c} = E\mathbf{c}$$

When solved, the smallest eigenvalue $E^{(0)}$ will yield the ground state energy, and $|\Psi_0\rangle$ can be found by considering the eigenvectors $\mathbf{c}^{(0)} = (C_0, C_i^a \ldots C_{ij}^{ab} \ldots \ldots C_{ij\ldots}^{ab\ldots})$. Excited states can also be found by considering the other eigenvalues and vectors $E^{(i)}, \mathbf{c}^{(i)}$.

FCI

Example, pairing interaction: $\hat{V}$ only works between spin-paired states at the same energy level. We let $p = 1, 2, 3, 4$ denote energy levels, with SP states also having a spin $\sigma = \pm$, a total of $n = 8$ SP states.

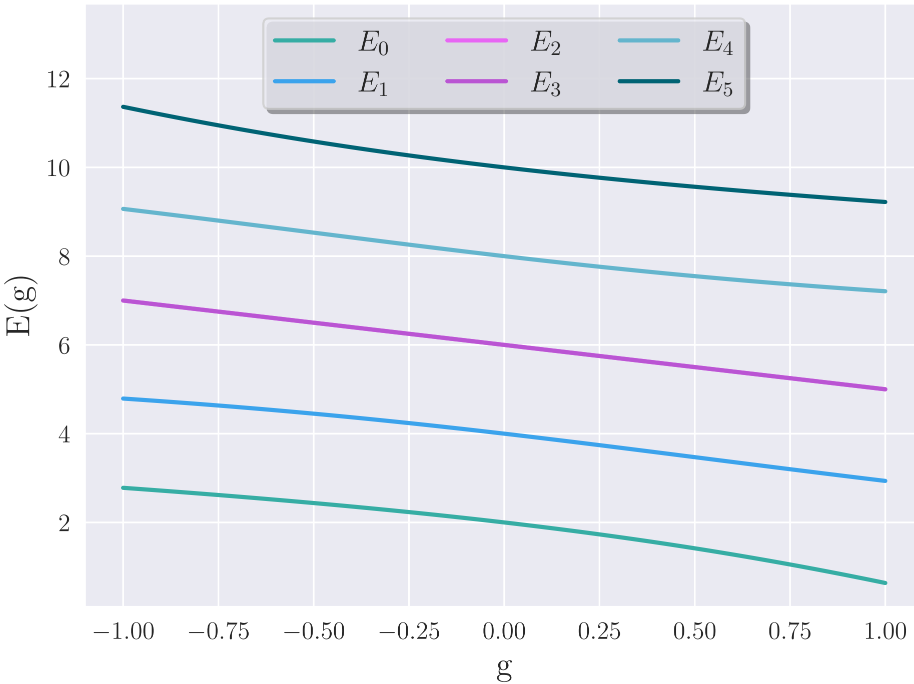
$$\hat{H} = \hat{H}_0 + \hat{V}, \qquad \hat{H}_0 = \sum_{p\sigma} (p-1) a^\dagger_{p\sigma} a_{p\sigma}, \qquad \hat{V} = -\frac{1}{2} g \sum_{pq} a^\dagger_{p+} a^\dagger_{p-} a_{q-} a_{q+}$$

Diagonal SP Hamiltonian $\hat{H}_0$ and two body interaction $\hat{V}$. Consider $N = 4$ particles with total spin $S = 0$, writing $|PQ\rangle = |p+p-q+q-\rangle$ we have a total of six different many body states.

0p0h	$\|12\rangle$
2p2h	$\|13\rangle, \|14\rangle, \|23\rangle, \|24\rangle$
4p4h	$\|34\rangle$

By setting up the matrix $\langle KL| \hat{H} |RS\rangle$, we get a small eigenvalue problem of a 6×6 matrix.

FCI



But there is a problem...

For all but very simple problems, this approach is unfeasible. In general, we have to consider

$$\binom{n}{N} = \frac{n!}{N!(n-N)!}$$

many body states. Taking our pairing model example, lifting the $S = 0$ restriction yields 70 different states. This is still possible, but increasing both n and N results in disaster

$N \downarrow / n \rightarrow$	8	32	64	128
4	70	10^4	10^5	10^7
8		10^7	10^9	10^{12}
16		10^8	10^{14}	10^{19}
32			10^{18}	10^{30}

Table. NB: Order of magnitude values

Pros:

- Provides exact solutions within a truncated basis set
- Understandable and relatively easy to set up
- Excited states thrown into the bargain

Cons:

- Computational complexity, bad scaling
- Only possible for tiny systems, with few states and particles.
- Practically only a benchmarking tool

Configuration Interaction (CI)

Follows the same methodology as FCI, but due to its large computational time, the many body states are also truncated.

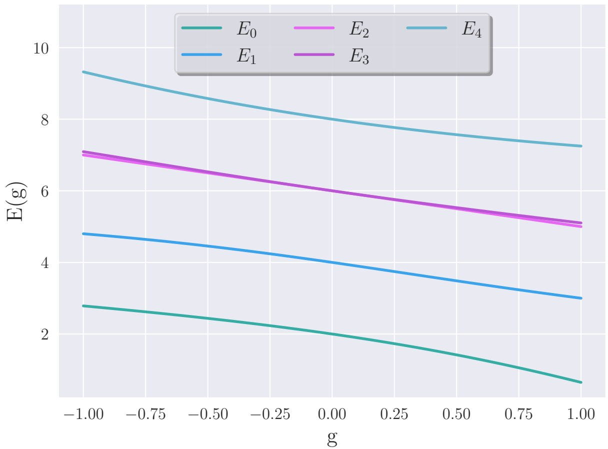
Different truncation levels can be chosen, for instance only include (in addition to $|\Phi_0\rangle$) 1p1h excitations (CIS) or 2p2h excitations (CID).

Truncation relies on an a priori ranking of the importance of different excited states, which contributions to include might not be obvious.

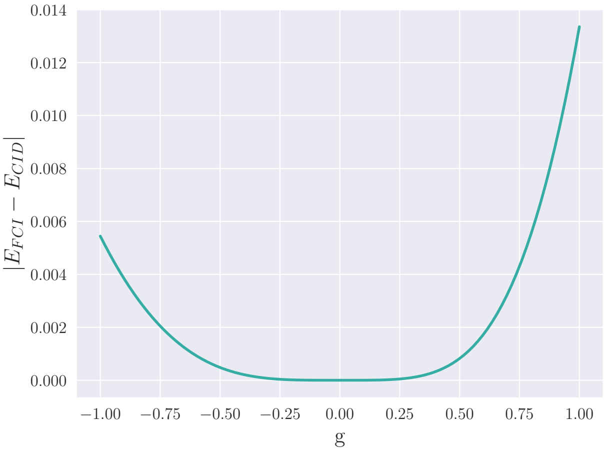
Considering our paring model example, we can exclude the 4p4h ($|34\rangle$) contributions from $\langle KL| \hat{H} |RS\rangle$, giving only the ground state ansatz and 2p2h excitations.

This reduces the matrix $6 \times 6 \rightarrow 5 \times 5$, showing how truncation is beneficial from a computational point of view.

CI



E_0
E_1
E_2
E_3
E_4
E(g)
g
10
8
6
4
2
−1.00 −0.75 −0.50 −0.25 0.00 0.25 0.50 0.75 1.00



$|E_{FCI} - E_{CID}|$
g
0.014
0.012
0.010
0.008
0.006
0.004
0.002
0.000
−1.00 −0.75 −0.50 −0.25 0.00 0.25 0.50 0.75 1.00

Pros:

- Understandable and relatively easy to set up
- Excited states thrown into the bargain
- Reduces the problem of FCI
- When adding contributions, we approach the exact energy (FCI).

Cons:

- Still quite computationally expensive
- Bad scaling for higher contributions
- What contributions to include might not be obvious
- Not size extensive

Hartree-Fock (HF)

Hartree-Fock methods approximate two body interactions as a mean field potential.
$|\Phi_0\rangle = a_1^\dagger, \ldots a_N^\dagger |0\rangle$.

$$E[\Phi^{\mathrm{HF}}] = \sum_i^N \langle i| h |i\rangle + \frac{1}{2}\sum_{ij}^N \langle ij| \hat{v} |ij\rangle_{\mathrm{AS}}$$

$$L[\Phi^{\mathrm{HF}}] = E[\Phi^{\mathrm{HF}}] - \sum_{pq}^n \epsilon_{pq}(\langle p|q\rangle - \delta_{pq})$$

HF

Pros:

- Cheap

Cons:

- Bad

Many body perturbation theory (MBPT)

Again, the exact ground state of the system is assumed to be an expansion of the ground state ansatz $|\Phi_0\rangle$ and excitations of this (1p1h, 2p2h...)

$$|\Psi_0\rangle = |\Phi_0\rangle + \sum_{m=1}^{\infty} C_m |\Phi_m\rangle$$

With m going over all $|\Phi_0\rangle$ excitations. There is no coefficient for $|\Phi_0\rangle$, since we have chosen intermediate normalization $\langle\Phi_0|\Psi_0\rangle = 1$. $|\Psi_0\rangle$ is an eigenstate of the full Hamiltonian and we subtract the Schrödinger equation from an arbitrary energy variable ω.

$$(\hat{H}_0 + \hat{V}) |\Psi_0\rangle = E |\Psi_0\rangle$$
$$(\omega - \hat{H}_0) |\Psi_0\rangle = (\omega - E + V) |\Psi_0\rangle$$

Defining two hermitian idempotent operators, for model space (P) and complimentary space (Q).

$$P = |\Phi_0\rangle \langle\Phi_0|, \quad Q = \sum_{m=1}^{\infty} |\Phi_m\rangle \langle\Phi_m|, \quad P^2 = P, Q^2 = Q, \quad [P, Q] = [\hat{H}_0, P] = [\hat{H}_0, Q] = 0$$

Together they for the identity in the complete Hilbert space $P + Q = I$, which is useful since

$$|\Psi_0\rangle = (P + Q) |\Psi_0\rangle = |\Phi_0\rangle + Q |\Psi_0\rangle$$
$$Q |\Psi_0\rangle = |\Psi_0\rangle - |\Phi_0\rangle$$

MBPT

When applying Q from the left, the rewritten Schrödinger equation becomes

$$Q\,|\Psi_0\rangle = \hat{R}_0(\omega)(\omega - E + V)\,|\Psi_0\rangle\,, \qquad \hat{R}_0(\omega) = \frac{Q}{\omega - \hat{H}_0}$$
$$|\Psi_0\rangle = |\Phi_0\rangle + \hat{R}_0(\omega)(\omega - E + V)\,|\Psi_0\rangle$$

This is solved iteratively, often starting with the guess $|\Psi_0^{(0)}\rangle = |\Phi_0\rangle$. The final state $|\Psi_0\rangle$ can then be expressed as.

$$|\Psi_0\rangle = \sum_{i=0}^{\infty} \left(\hat{R}_0(\omega)(\hat{V} - E + \omega)\right)^i |\Phi_0\rangle$$

With an energy:

$$E = \langle\Phi_0|\,\hat{H}_0 + \hat{V}\,|\Psi_0\rangle = E^{(0)} + \Delta E = E^{(0)} + \sum_{i=0}^{\infty} \langle\Phi_0|\,\hat{V}\left(\hat{R}_0(\omega)(\hat{V} - E + \omega)\right)^i |\Phi_0\rangle$$

Taking just the correlation energy ΔE, we define the PT order by where we truncate this contribution

$$\Delta E = \sum_{i=0}^{\infty} \Delta E^{(i)}, \qquad \Delta E^{(i)} = \langle\Phi_0|\,\hat{V}\left(\hat{R}_0(\omega)(\hat{V} - E + \omega)\right)^i |\Phi_0\rangle$$

Different approaches, Rayleigh-Schrödinger (RS)

Different choices of ω can now be made in order to obtain different types of PT expansions.

Setting $\omega = E$ removes E from $(\hat{V} - E + \omega)$, but it is still present in $\hat{R}_0(\omega = E)$, giving an implicit equation. This approach is called Brillouin-Wigner (BW) PT.

Setting $\omega = E^{(0)}$, we do not have the E dependence problem for $\hat{R}_0$, and by setting $\Delta E = E - E^{(0)}$ we obtain.

$$\Delta E = \sum_{i=0}^{\infty} \Delta E^{(i)} = \sum_{i=0}^{\infty} \langle \Phi_0 | \hat{V} \left(\hat{R}_0(\omega)(\hat{V} - \Delta E) \right)^i | \Phi_0 \rangle$$

This does not seem to bring any improvement, since we still have an implicit equation. However, since $\hat{R}_0$ contains Q and ΔE is just a scalar, $\hat{R}_0 \Delta E | \Psi_0 \rangle = \Delta E \hat{R}_0 | \Psi_0 \rangle = 0$, a pretty neat perturbative expansion can be formed when gathering terms of the same interaction order.

Explicitly, we expand ΔE

$$\begin{aligned}
\Delta E &= \langle\Phi_0|\,\hat{V}\,|\Phi_0\rangle + \langle\Phi_0|\,\hat{V}\hat{R}_0(\hat{V}-\Delta E)\,|\Phi_0\rangle + \langle\Phi_0|\,\hat{V}\hat{R}_0(\hat{V}-\Delta E)\hat{R}_0(\hat{V}-\Delta E)\,|\Phi_0\rangle + \ldots \\
&= \langle\Phi_0|\,\hat{V}\,|\Phi_0\rangle + \langle\Phi_0|\,\hat{V}\hat{R}_0\hat{V}\,|\Phi_0\rangle + \langle\Phi_0|\,\hat{V}\hat{R}_0(\hat{V}-\Delta E)\hat{R}_0\hat{V}\,|\Phi_0\rangle + \ldots \\
&= E^{(1)} + E^{(2)} + \langle\Phi_0|\,\hat{V}\hat{R}_0\hat{V}\hat{R}_0\hat{V}\,|\Phi_0\rangle - \langle\Phi_0|\,\hat{V}\hat{R}_0\Delta E\hat{R}_0\hat{V}\,|\Phi_0\rangle + \ldots
\end{aligned}$$

And by inserting recursively for ΔE, we get *two* terms with three $\hat{V}$s, giving $E^{(3)}$. Higher orders of $\hat{V}$ will be given to $E^{(4)}, E^{(5)}, \ldots$.

$$\begin{aligned}
&\langle\Phi_0|\,\hat{V}\hat{R}_0\hat{V}\hat{R}_0\hat{V}\,|\Phi_0\rangle - \langle\Phi_0|\,\hat{V}\hat{R}_0(E^{(1)} + E^{(2)} + \ldots)\hat{R}_0\hat{V}\,|\Phi_0\rangle + \ldots \\
=&\left(\langle\Phi_0|\,\hat{V}\hat{R}_0\hat{V}\hat{R}_0\hat{V}\,|\Phi_0\rangle - E^{(1)}\langle\Phi_0|\,\hat{V}\hat{R}_0^2\hat{V}\,|\Phi_0\rangle\right) - E^{(2)}\langle\Phi_0|\,\hat{V}\hat{R}_0^2\hat{V}\,|\Phi_0\rangle + \ldots \\
=&E^{(3)} - E^{(2)}\langle\Phi_0|\,\hat{V}\hat{R}_0^2\hat{V}\,|\Phi_0\rangle + \ldots
\end{aligned}$$

We can now use this as a normal perturbative series that can be truncated at a specific interaction order (RS2, RS3 and so on).

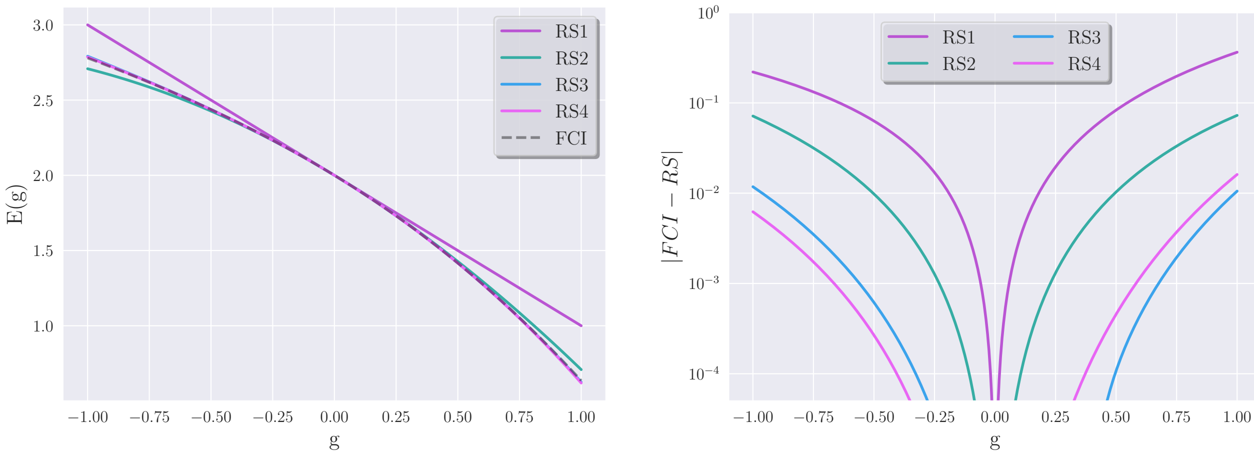
In contrast to CI/Hartree-Fock, this is not a variational approach. There is no guarantee for convergence and results across different orders can vary.

If the SP energies are very close ($\hat{H}_0$), convergence might be a problem since the denominator of $\hat{R}_0$ can explode.

$$E^{(2)} = \langle\Phi_0|\,\hat{V}\hat{R}_0\hat{V}\,|\Phi_0\rangle = \sum_m{}' \langle\Phi_0|\,\hat{V}\frac{|\Phi_m\rangle\,\langle\Phi_m|}{E^{(0)} - \hat{H}_0}\hat{V}\,|\Phi_0\rangle = \frac{1}{4}\sum_{ijab}\frac{|\,\langle ij|\,\hat{v}\,|ab\rangle\,|^2}{\epsilon_i + \epsilon_j - \epsilon_a - \epsilon_b}$$

If the interaction is parametrized by a coupling constant, the coupling/SP energy ratio is crucial.

RS



RS1
RS2
RS3
RS4
FCI
E(g)
g
3.0
2.5
2.0
1.5
1.0
−1.00
−0.75
−0.50
−0.25
0.00
0.25
0.50
0.75
1.00
RS1
RS3
RS2
RS4
|FCI − RS|
g
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}

Pros:

- Cheap compared with CI methods
- Still capable of high accuracy
- Incorporate high order excitations, even at low order
- Size extensive

Cons:

- No guaranty for convergence
- Nonvariational, we have no energy bounds
- Degeneracy (at least this formulation)

These examples follow the Metropolis Theme

- Regular
- Alert
- *Italic*
- **Bold**

Items

- Cats
  - British Shorthair
- Dogs
- Birds

Enumerations

1. First
   1.1 First subpoint
2. Second
3. Last

Descriptions

Apples Yes
Oranges No
Grappes No

Table. Largest cities in the world (source: Wikipedia)

City	Population
Mexico City	20,116,842
Shanghai	19,210,000
Peking	15,796,450
Istanbul	14,160,467

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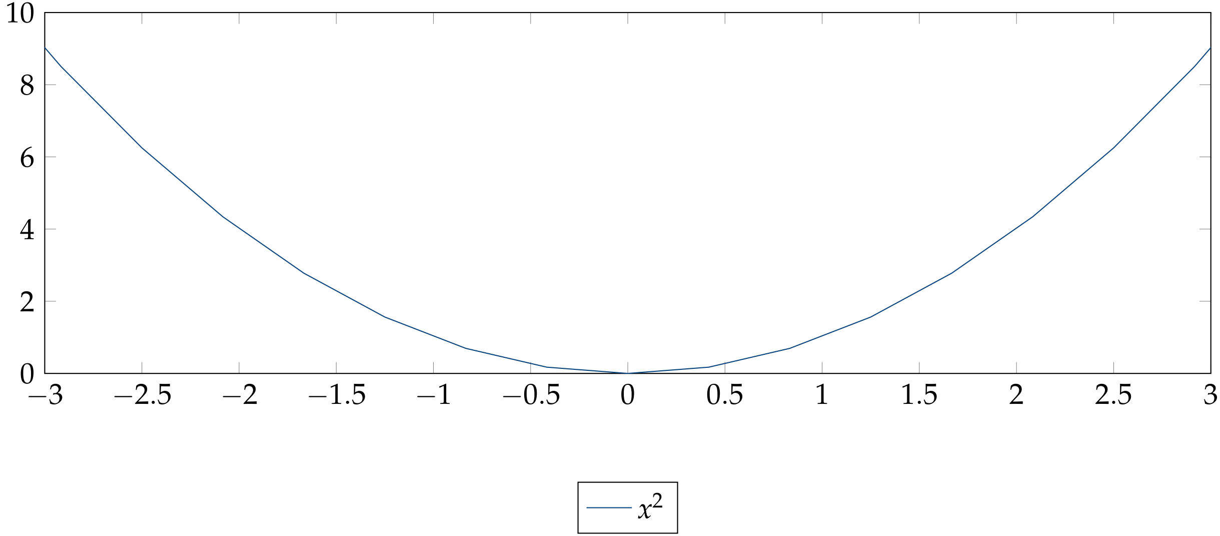
Figure. Plot of $y = x^2$



Default

Block content.

Alert

Block content.

Example

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Maths

Equations

- A numbered equation:

$$y_t = \beta x_t + \varepsilon_t \tag{1}$$

- Another equation:

$$\mathbf{Y} = \boldsymbol{\beta}\mathbf{X} + \boldsymbol{\varepsilon}_t$$

- Theorems are numbered consecutively.

Theorem 1 (Example Theorem)

Given a discrete random variable X, which takes values in the alphabet $\mathcal{X}$ and is distributed according to $p : \mathcal{X} \to [0, 1]$:

$$\mathrm{H}(X) := -\sum_{x \in \mathcal{X}} p(x) \log p(x) = \mathbb{E}[-\log p(X)] \tag{2}$$

- Definition numbers are prefixed by the section number in the respective part.

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Part I

Demo Presentation Part 2

References I