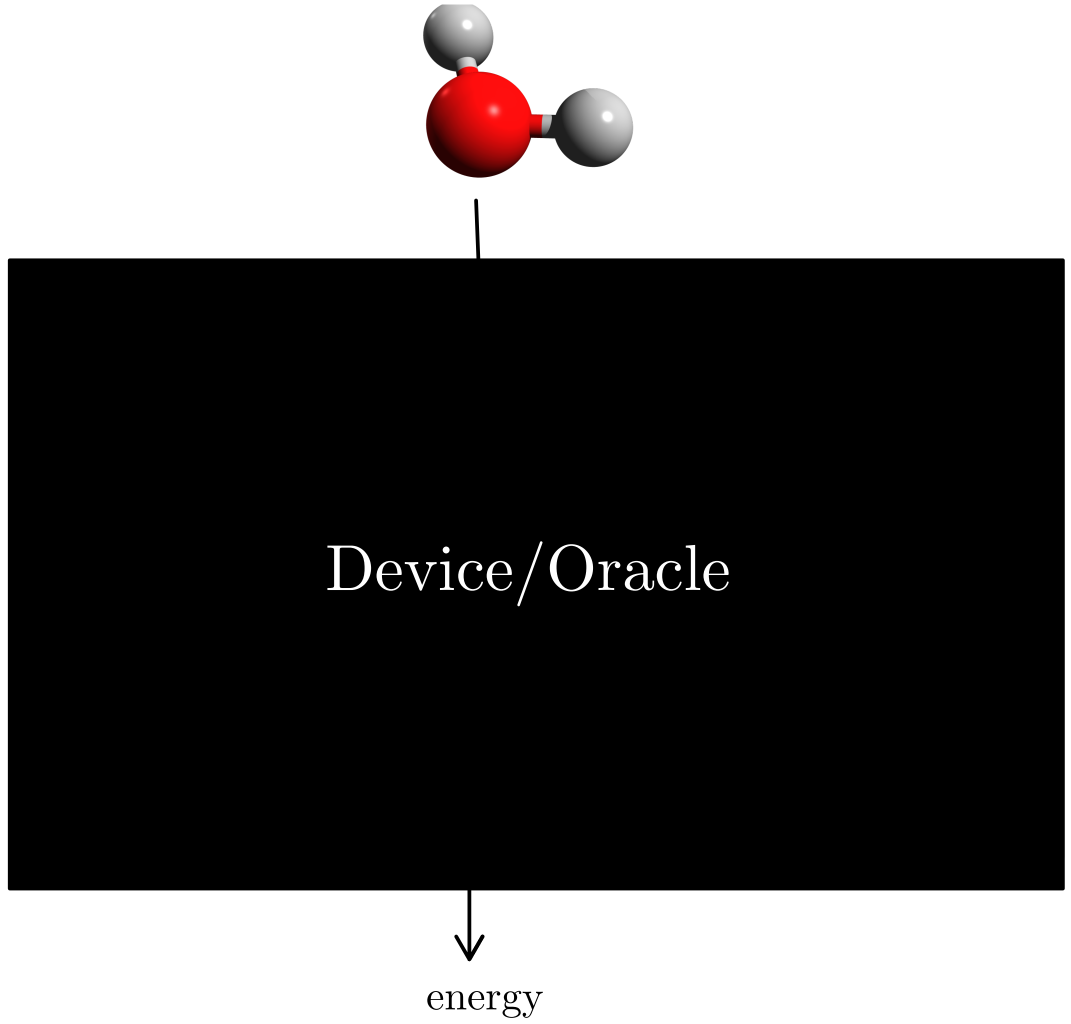
the matter lab

# Quantum Algorithms for Chemistry, Physics and Beyond

Jakob S. Kottmann

VELUT ARBOR ÆVO

# Quantum Chemistry in a Nutshell



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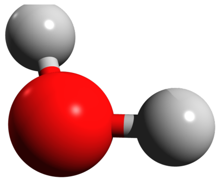


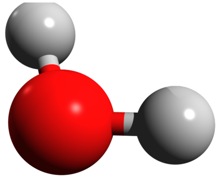
$\rightarrow$ coordinates and charges $\rightarrow \{R_k, Z_k\} \rightarrow V(r) = -\sum_k \frac{Z_k}{\|r - R_k\|}$

Device/Oracle

$\downarrow$

energy

# Quantum Chemistry in a Nutshell



$\rightarrow$ coordinates and charges $\rightarrow \{R_k, Z_k\} \rightarrow V(r) = -\sum_k \frac{Z_k}{\|r - R_k\|}$

real-space Hamiltonian

$$H(r_0, \ldots, r_9) = -\sum_i \left( \frac{\nabla^2_{r_i}}{2} + V(r_i) \right) + \sum_{i<j} \frac{1}{\|r_i - r_j\|}$$

↓

discretize

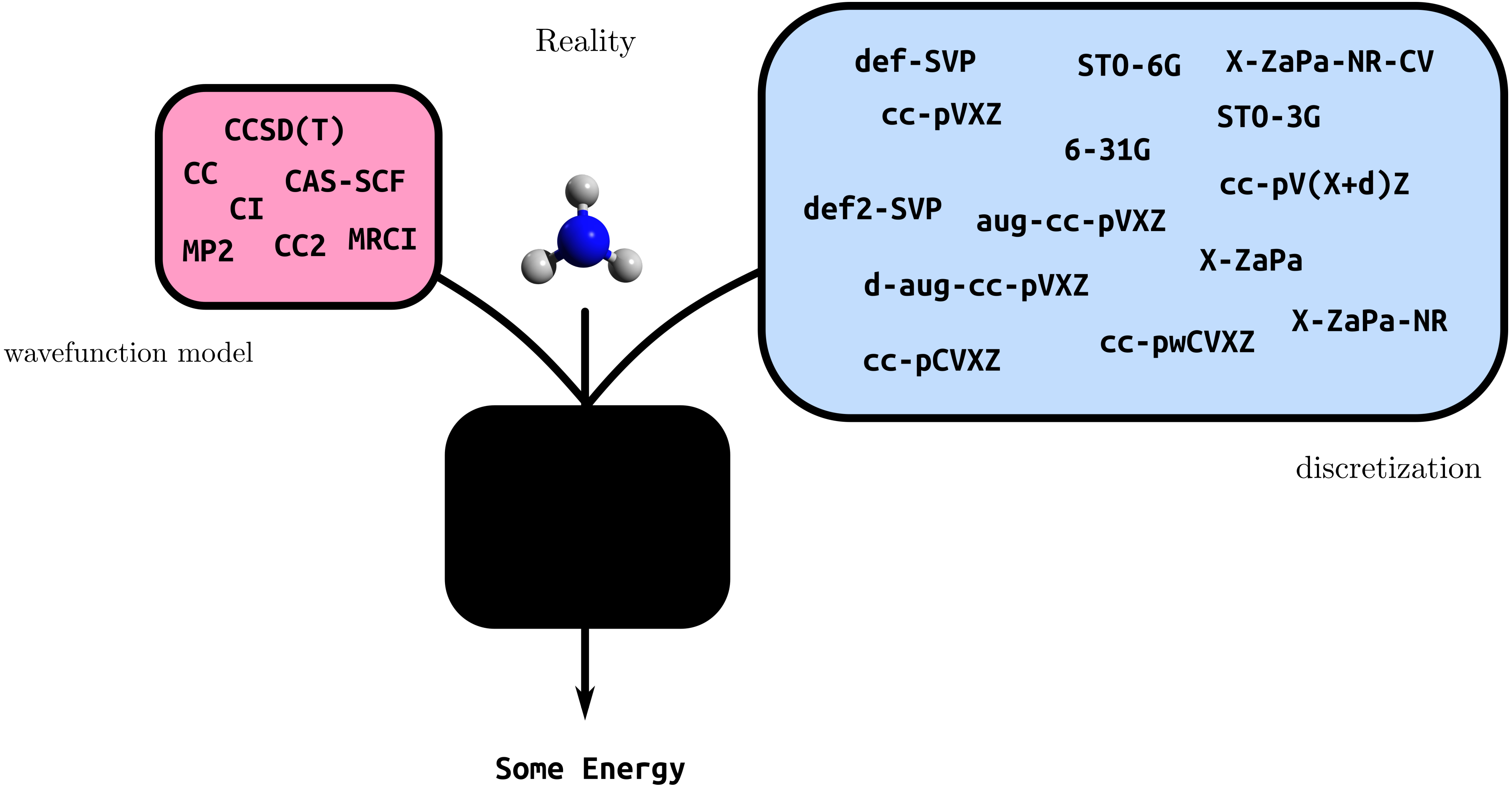
↓

wavefunction model

↓

energy

# Quantum Chemistry in a Nutshell



# Many-Body Physics: Splitting the Task

N-Body Problem

$$H(x,y) = -\frac{1}{2}\frac{\partial^2}{\partial x^2} - \frac{1}{2}\frac{\partial^2}{\partial y^2} + \frac{1}{\|x-y\|} + f(x) + f(y)$$

Example: 2-Body Hamiltonian

JSK, Schleich, Tamayo-Mendoza, Aspuru-Guzik. J.Chem.Phys.Lett. 2021

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Example: 2-Body Hamiltonian

Classical Domain

effective one/two-body problems

$$F(x) = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + V(x,\phi)$$

$$F(x)\phi_k(x) = a_k\phi_k(x)$$

JSK, Schleich, Tamayo-Mendoza, Aspuru-Guzik. J.Chem.Phys.Lett. 2021

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**Classical Domain**

effective one/two-body problems

$$F(x) = -\frac{1}{2}\frac{\partial^2}{\partial x^2} + V(x,\phi)$$

$$F(x)\phi_k(x) = a_k\phi_k(x)$$

→ determine $\phi_k$

qubit encoding

**Quantum Domain**

Example:

$|1001\rangle \rightarrow \phi_0$ and $\phi_3$ occupied with an electron

qubit Hamiltonian

$$H = \sum_k c_k P_k$$

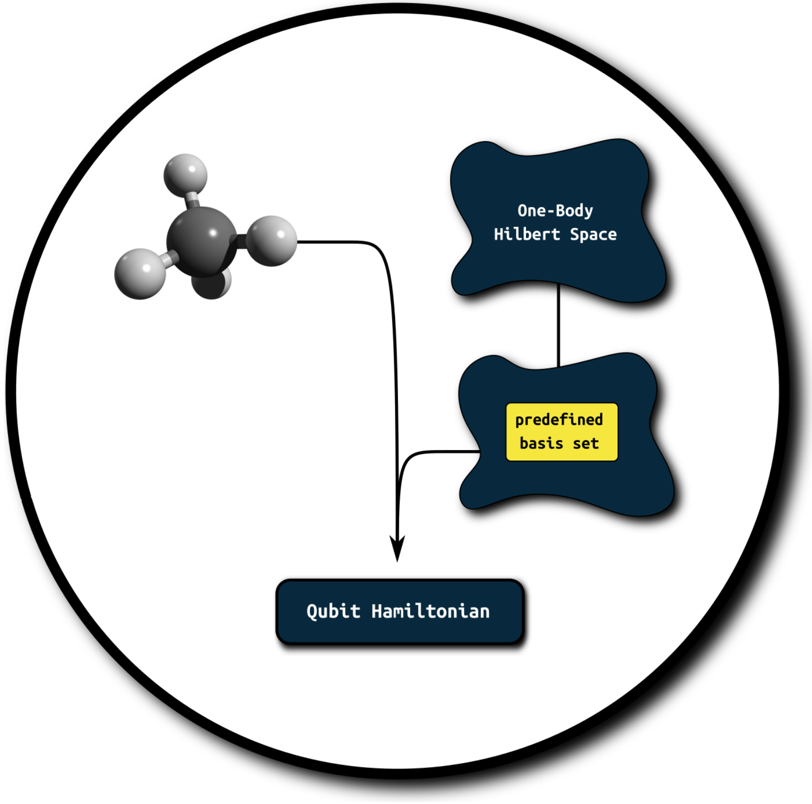
solve for ground state

← feedback: refine $V(x,\phi)$

JSK, Schleich, Tamayo-Mendoza, Aspuru-Guzik. J.Chem.Phys.Lett. 2021

# Many-Body Physics: Splitting the Task

Traditional Approach



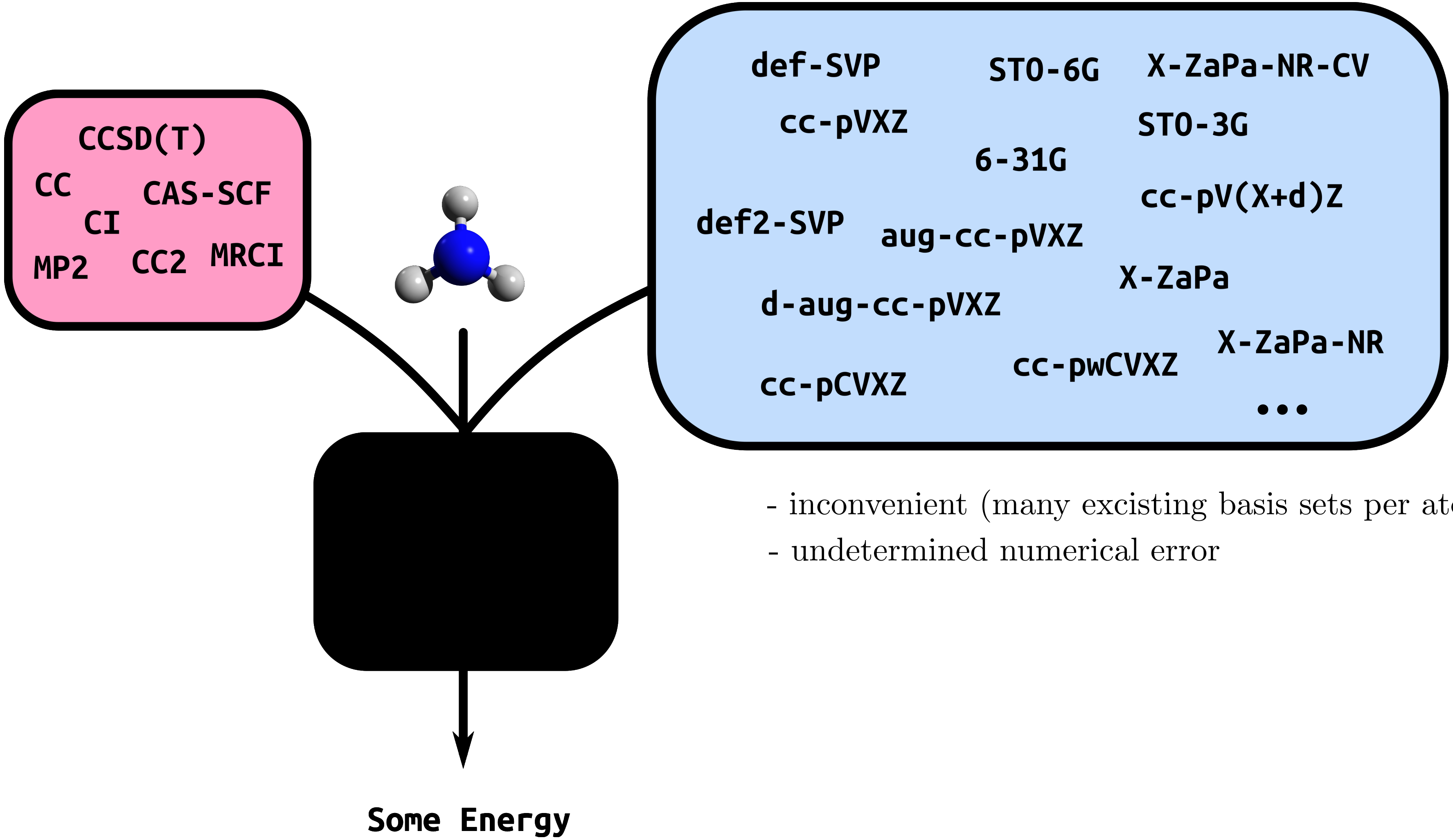

Advantages

- well established
- fast integrals

Drawbacks

- no black-box
- inconvenient (many excisting basis sets per atom)
- more qubits necessary
- undetermined numerical error

# Many-Body Physics: Splitting the Task

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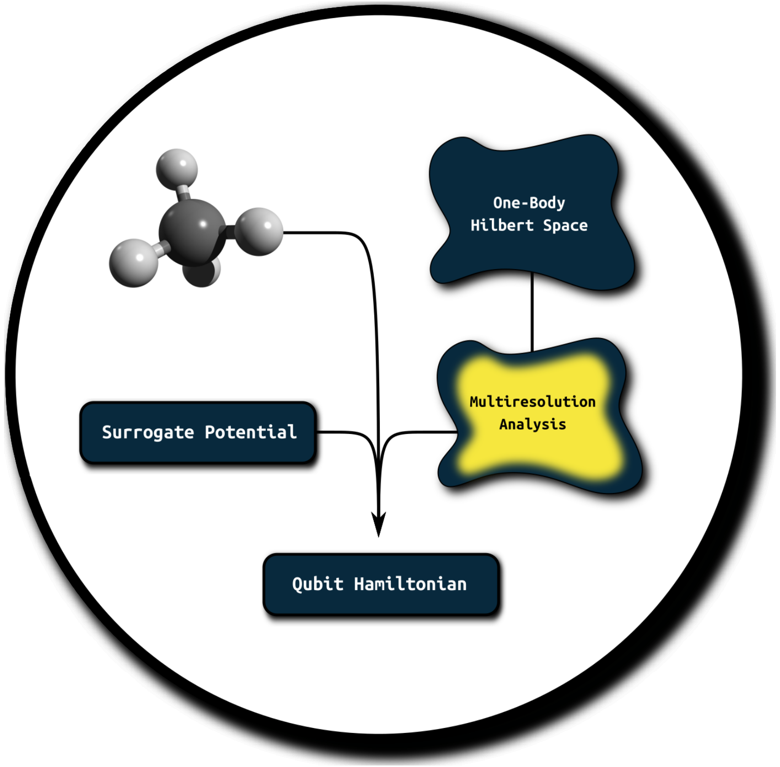
# Many-Body Physics: Splitting the Task

System-Adapted Approach




Advantages

- defined numerical error
- can be treated as black-box
- low qubit numbers

Drawbacks

- not well established
- comparably high classical computational cost

  formal scaling is often better though

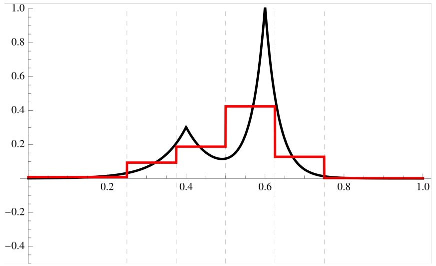
high-level blog article:

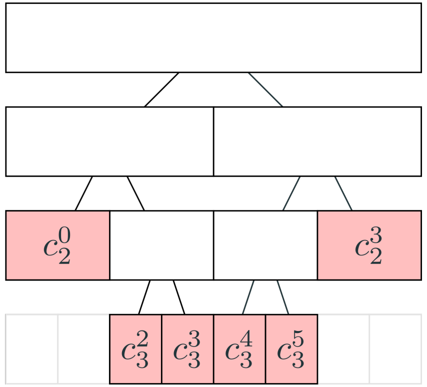
https://aspuru.substack.com/p/bits-are-cheap-and-qubits-expensive

JSK, Schleich, Tamayo-Mendoza, Aspuru-Guzik. J.Chem.Phys.Lett. 2021

# System Adapted Approach: Behind the Scenes

1 Dimensional Example




$$|f\rangle = \sum_{nl} c_n^l |\varphi_n^l\rangle$$

**github/madness**
Harrison et. al.

R.J. Harrison *et.al* SIAM 2016

Review (classical methods): F.A. Bischoff Adv. Quant. Chem. 2019

JSK, F. A. Bischoff, E. F. Valeev. J. Chem. Phys. 2020

Direct 2-body approach: JSK, F. A. Bischoff, J. Chem. Theo. & Comp. 2018

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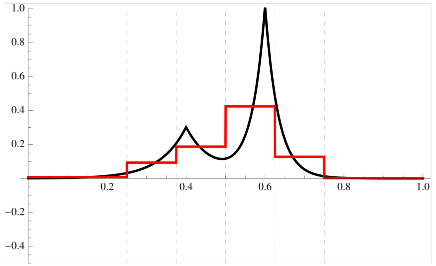


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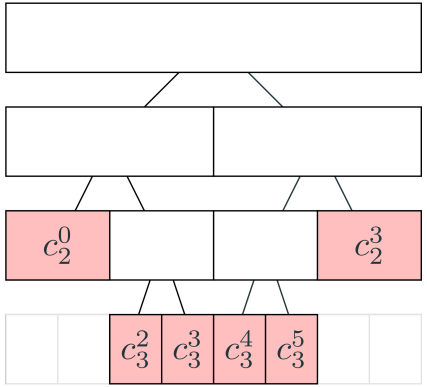
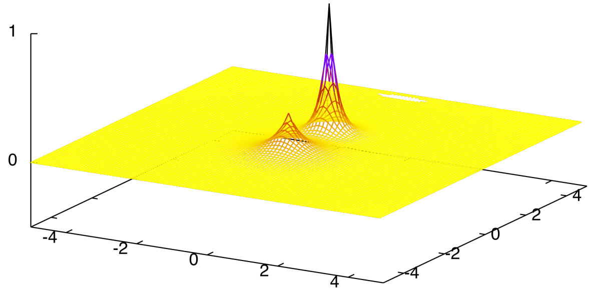
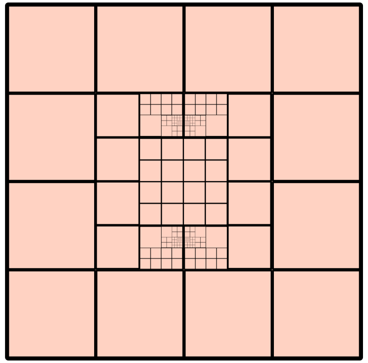



## 2 Dimensional Example



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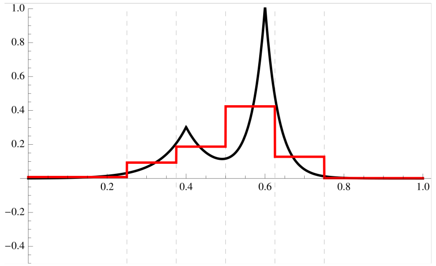


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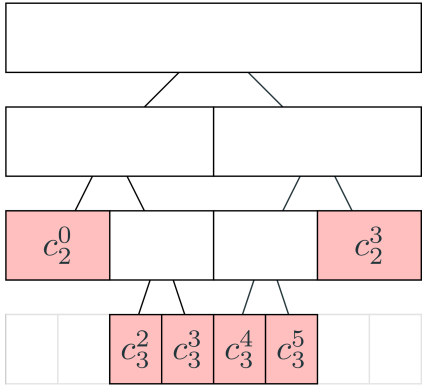
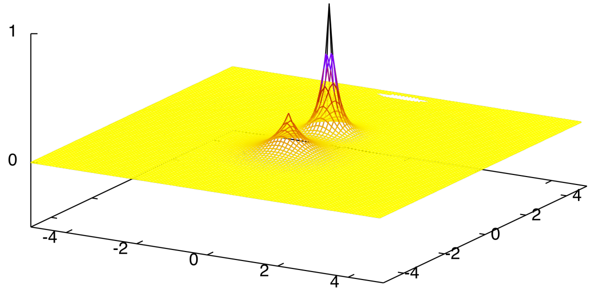
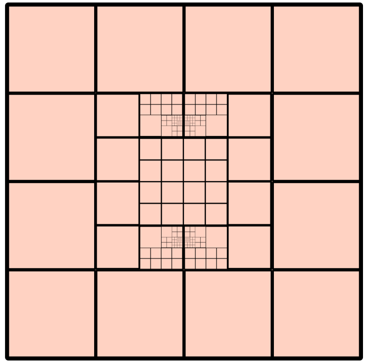



2 Dimensional Example



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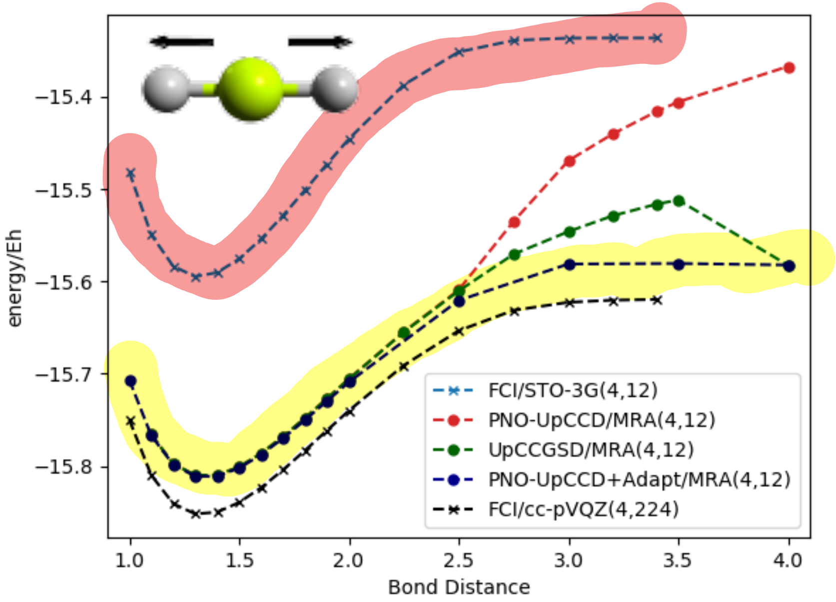
# Basis-Set-Free Quantum Chemistry: Performance

System-Adapted Approach

Traditional Approach

| System | Metric | MRA | GBS |
|---|---|---|---|
| He | MAX | **4** | 4-10 |
| Be | MAX | **10** | 10-18 |
| $H_2$ | NPE | **4** | 20-56 |
| $H_2$ | NPE | **8** | 20-56 |
| $H_2$ | NPE | **20** | 56-120 |
| $H_2$ | MAX | **4** | 8 |
| $H_2$ | MAX | **8** | 20-56 |
| $H_2$ | MAX | **20** | 56 |
| LiH | NPE | **12-22** | 38-88 |
| LiH | MAX | **12** | 38-88 |
| LiH | MAX | **22** | 170-288 |
| BH | NPE | **12-22** | 38-88 |
| BH | MAX | **12-22** | 38-88 |
| $BeH_2$ | NPE | **12** | 46-114 |
| $BeH_2$ | MAX | **12** | 24-46 |
| $NH_3$ | $\Delta E$ | **12-18** | 58-100 |




high-level blog article:

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JSK, Schleich, Tamayo-Mendoza, Aspuru-Guzik. J.Chem.Phys.Lett. 2021

what about the wavefunction model?

one way forward: quantum circuits

# Quantum Circuits

Task: Implement a unitary evolution

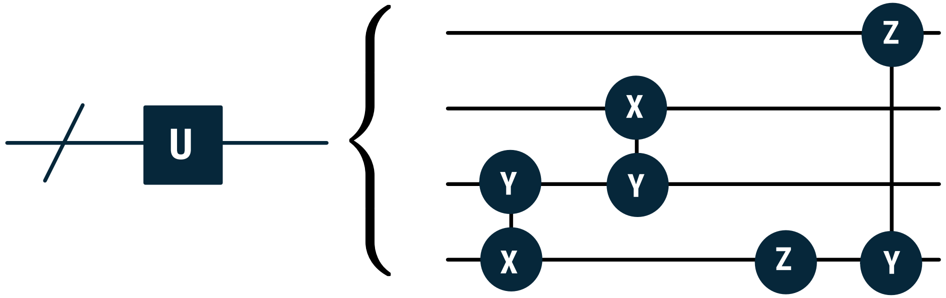
$$U = e^{i\theta G}$$

$G$ is Hermitian 1 or 2 qubit operator

$\theta \in \mathbb{R}$ free parameter

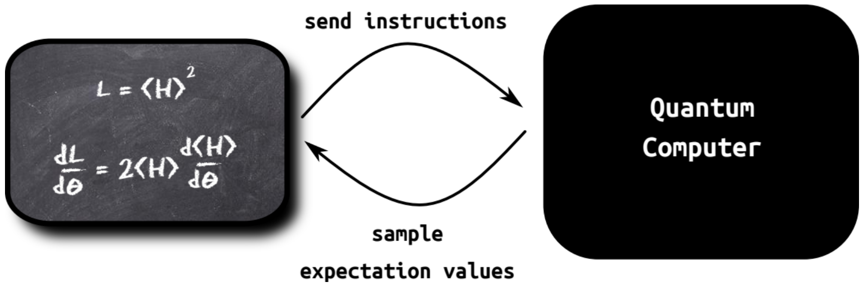
Can be automatically differentiated

pioneers: M. Schuld *et.al* PRA 2019, Pennylane



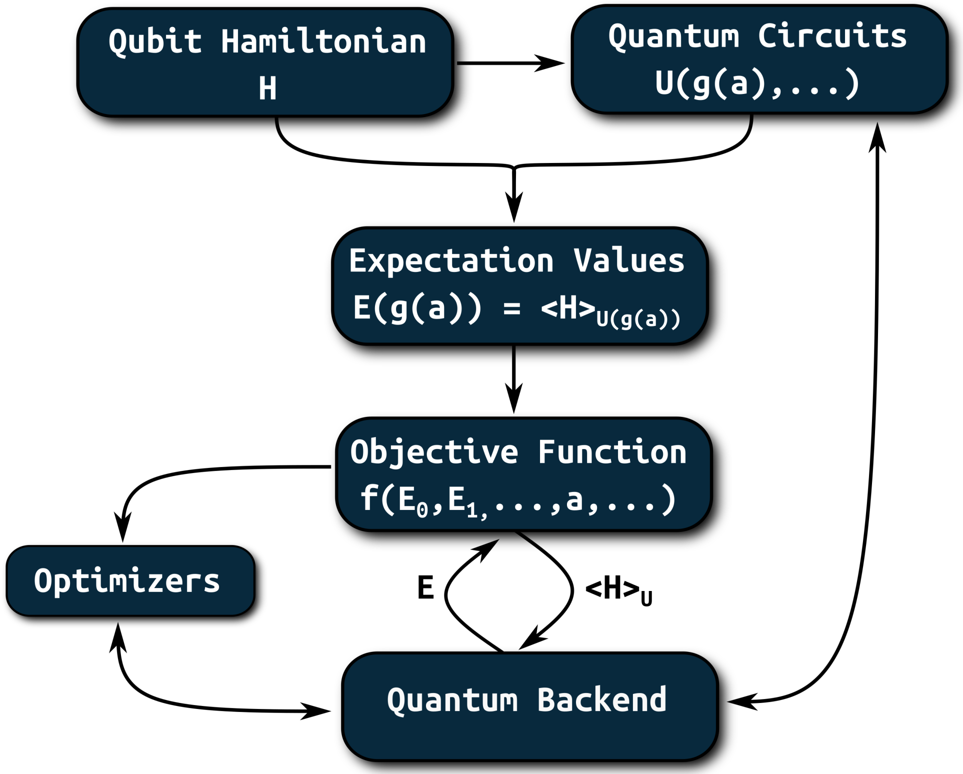

Optimizing quantum circuits: VQE (McClean et.al.) and QAOA (Farhi et.al.)

# Tequila: High Level Environment

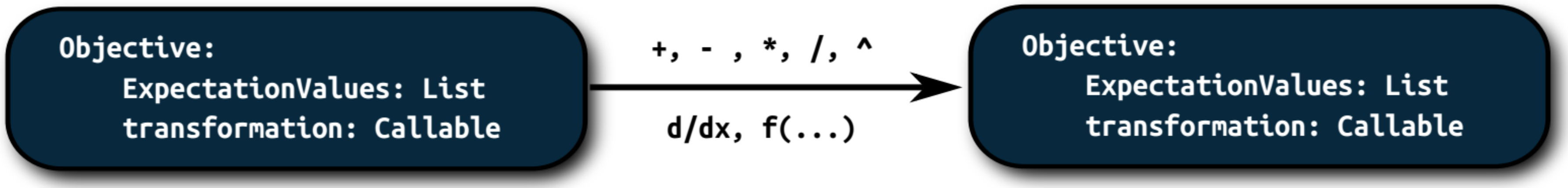



github.com/aspuru-guzik-group/tequila

API inspired by madness library




JSK, S. Alperin-Lea, A. Cervera-Lierta, T. Tamayo-Mendoza, et. al. Quant. Science & Technology 2021 concept



Objective:
ExpectationValues: List
transformation: Callable
+, - , *, /, ^
d/dx, f(...)
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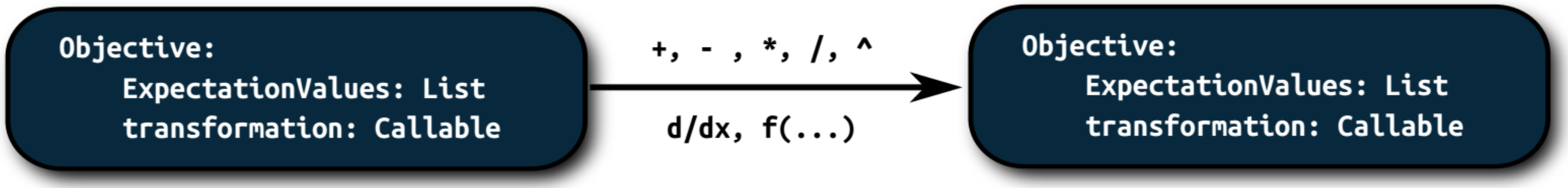
ExpectationValues: List
transformation: Callable

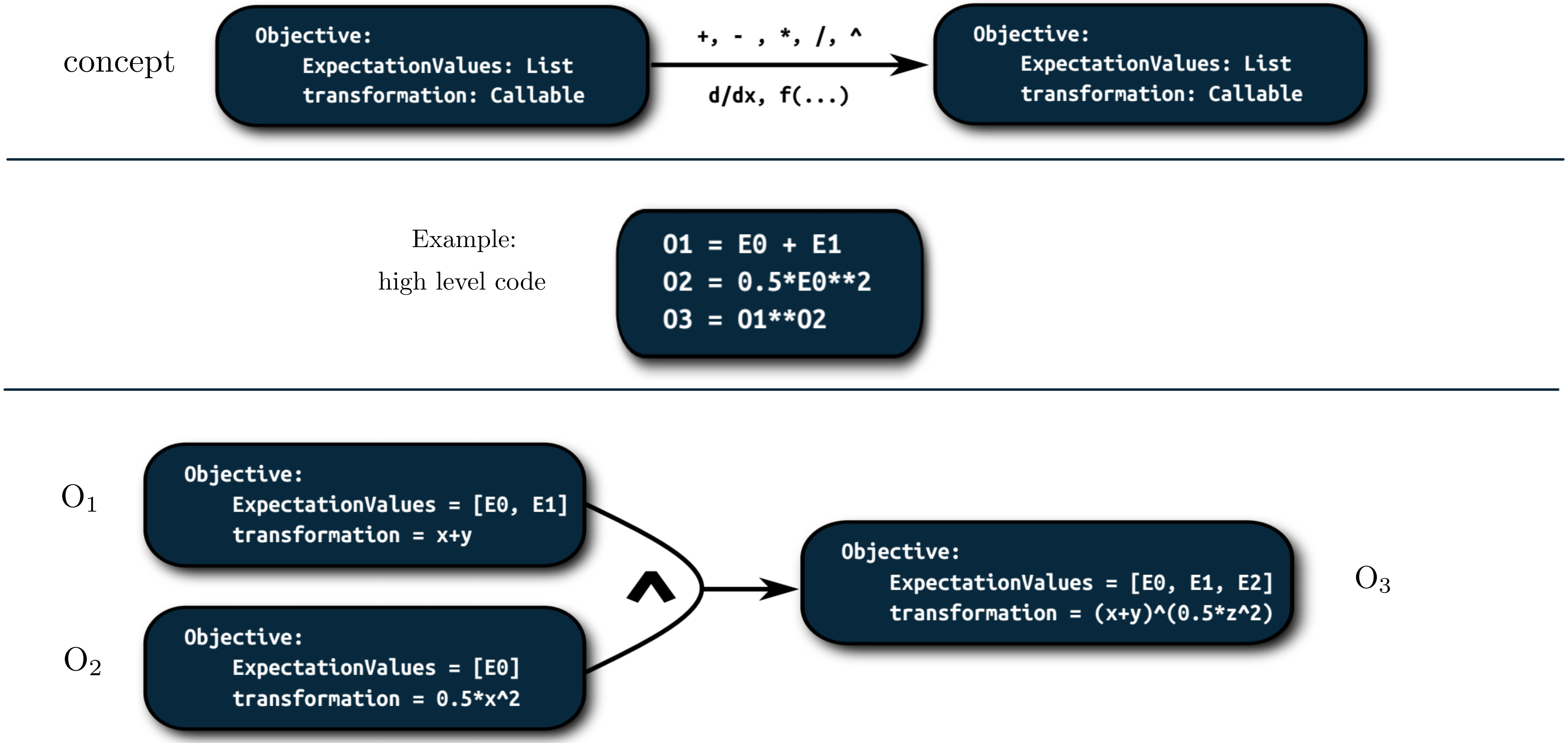
concept




Example:

high level code

```
O1 = E0 + E1
O2 = 0.5*E0**2
O3 = O1**O2
```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Objective:
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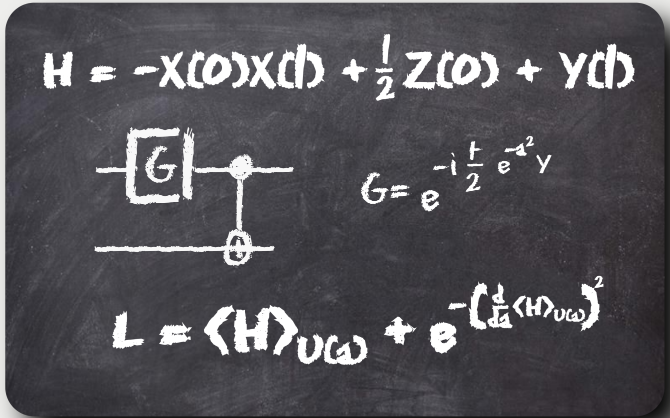
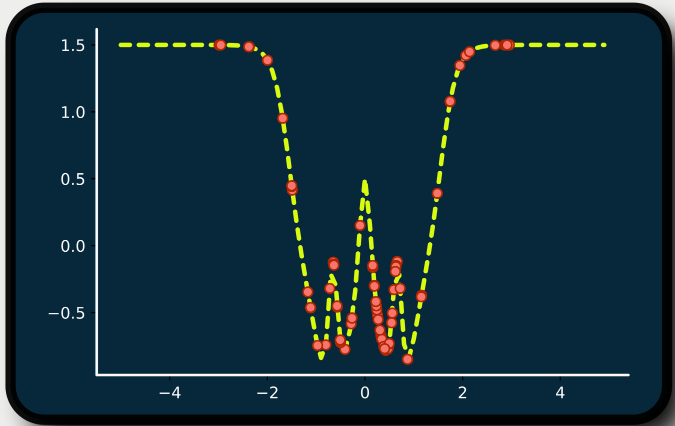
Objective:
ExpectationValues: List
transformation: Callable
Example:
high level code
O1 = E0 + E1
O2 = 0.5*E0**2
O3 = O1**O2
O1
Objective:
ExpectationValues = [E0, E1]
transformation = x+y
O2
Objective:
ExpectationValues = [E0]
transformation = 0.5*x^2
^
Objective:
ExpectationValues = [E0, E1, E2]
transformation = (x+y)^(0.5*z^2)
O3

# Tequila: High Level Environment




```
a = tq.Variable("a")
U = tq.gates.Ry(angle=(-a**2).apply(tq.numpy.exp)*pi, target=0)
U += tq.gates.X(target=1, control=0)
H = tq.QubitHamiltonian.from_string("-1.0*X(0)X(1)+0.5Z(0)+Y(1)")
E = tq.ExpectationValue(H=H, U=U)
dE = tq.grad(E, "a")
objective = E + (-dE**2).apply(tq.numpy.exp)
result = tq.minimize(method="phoenics", objective=objective)
```

# Some Development Examples

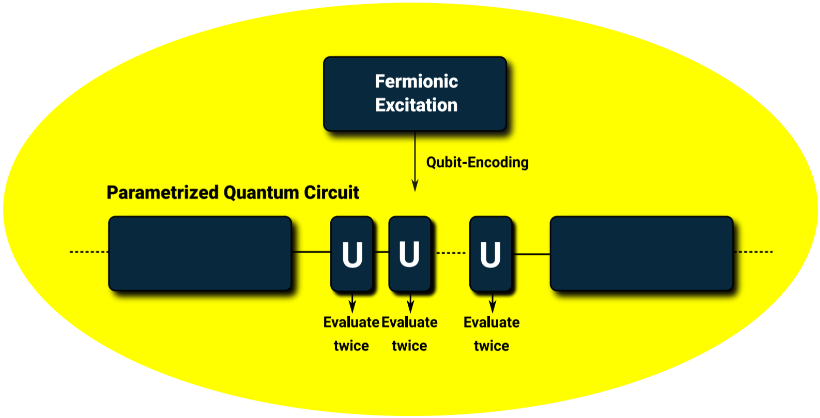
# Development Example: Advanced Gradients for Quantum Chemistry

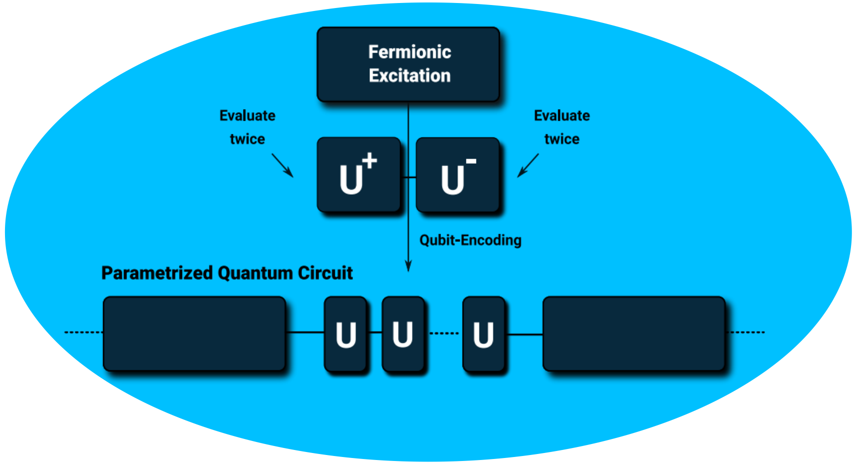
gradient cost for $n$ electron excitation

| Generator Form | Gradient Cost | Strategy |
|---|---|---|
| $G_{\mathbf{pq}} = \sum_{\mathbf{i}} c_{\mathbf{i}} \sigma_{\mathbf{i}}$ | $\mathcal{O}\left(2^{2n}\right)$ | shift-rule Eq. (6) |
| $G_{\mathbf{pq}} = \frac{1}{2}\left(G_{+} + G_{-}\right)$ | 4 | fermionic-shift Eq. (16) |
| Real Wavefunctions | | |
| $G_{\mathbf{pq}} = \frac{1}{2}\left(G_{+} + G_{-}\right)$ | 2 | fermionic-shift Eq. (19) |
| Generator Approximation | | |
| $G_{\mathbf{pq}} \approx G_{\pm}$ | 2 | shift-rule Eq. (6) |

Basic building blocks for Unitary Coupled-Cluster

recent review: A. Anand *et.al*. 2021




$\rightarrow$ generalizable

follow-ups:

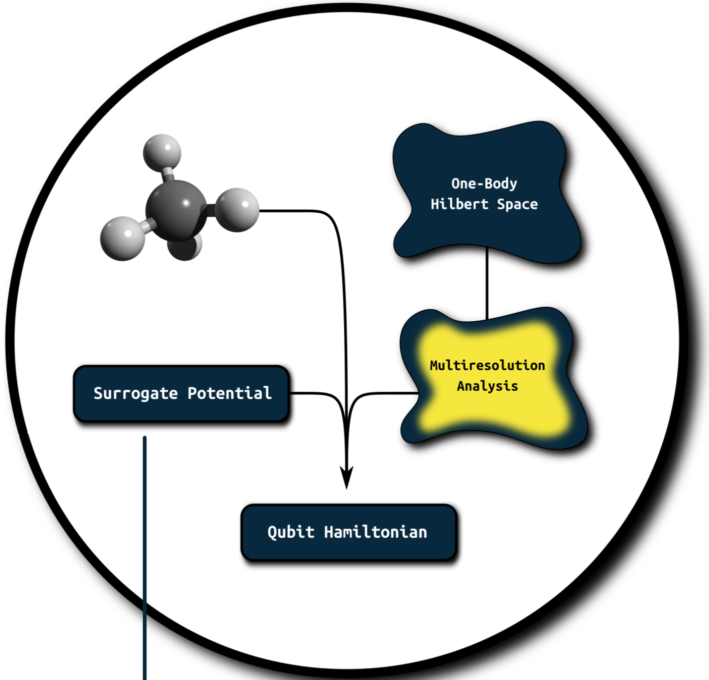
Izmaylov *et.al*. 2021

Anselmetti *et.al*. 2021

Wierichs *et.al*. 2021

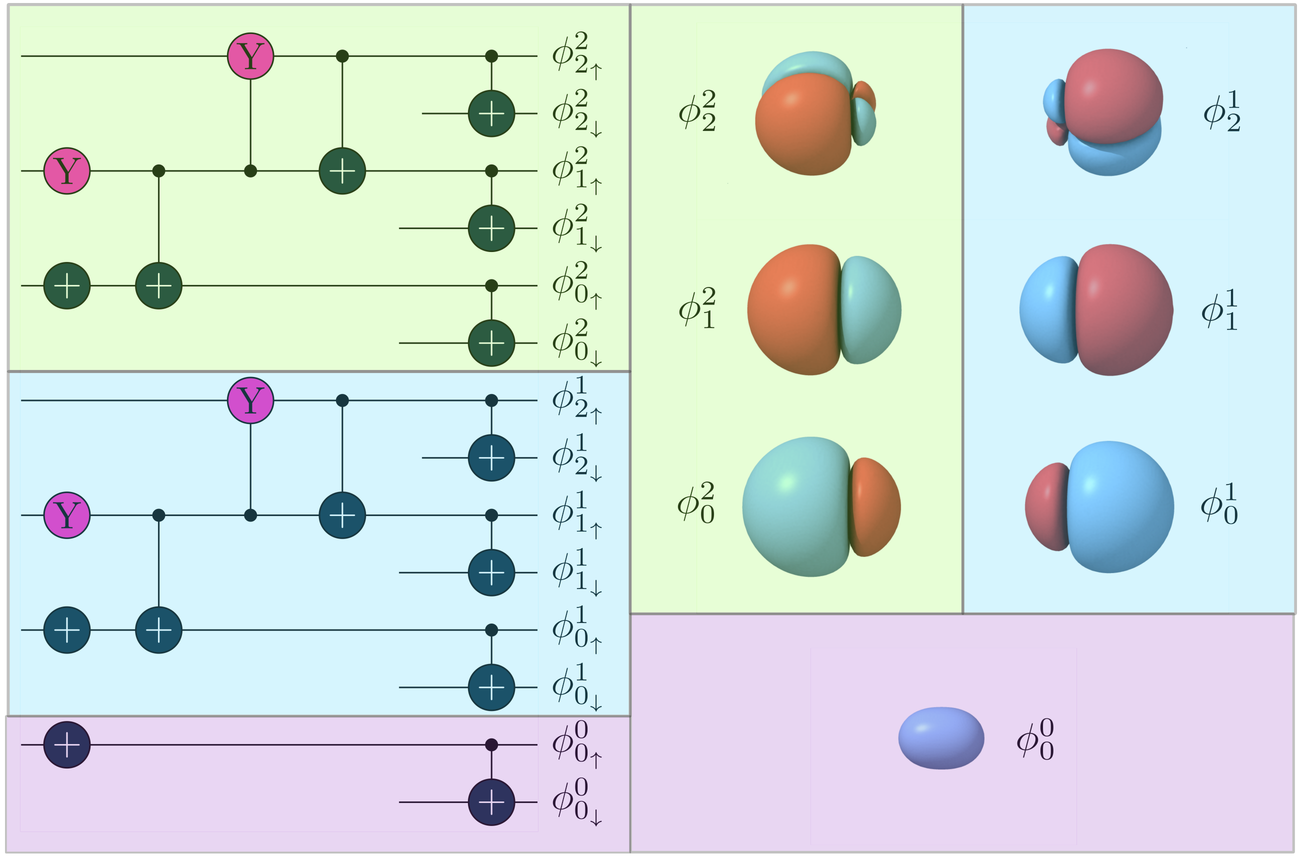
JSK, A. Anand, A. Aspuru-Guzik. Chemical Science 2021

# Development Example: Separable Pair Approximations




exploit physical insight

High level circuit design through physical principles




JSK, A. Aspuru-Guzik, Arxiv:2105.03836, 2021

# Development Example: Separable Pair Approximations

classically simulatable

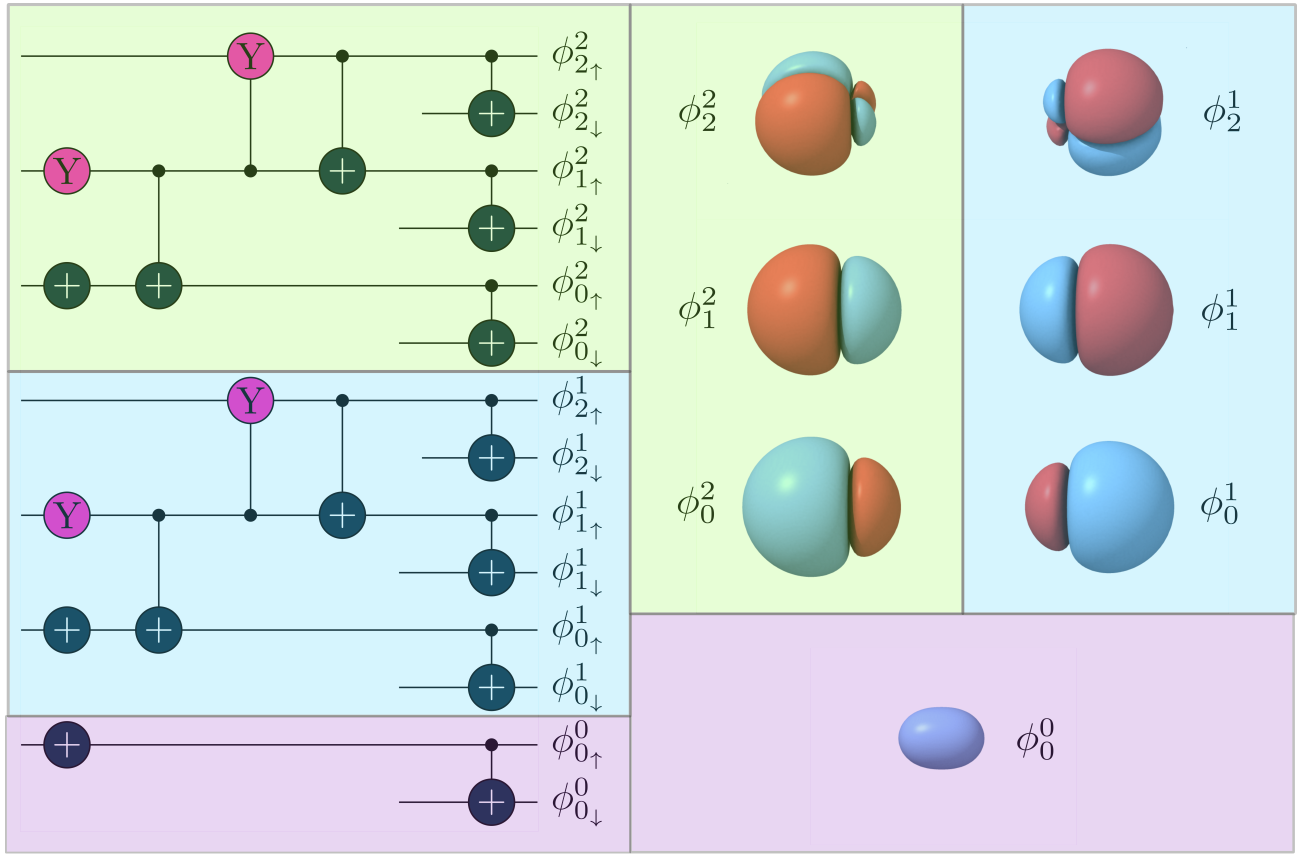
→ cheap initial states

separated pairs

→ distributed schemes

→ hybrid simulation

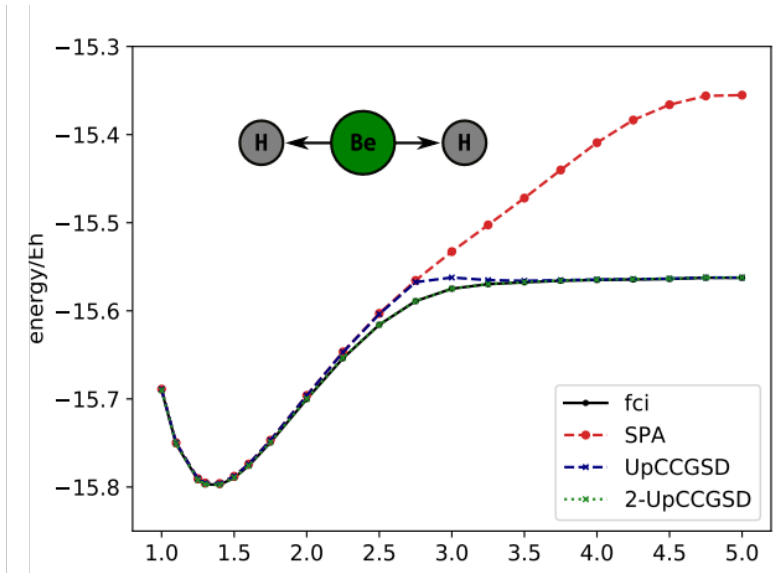
High level circuit design through physical principles



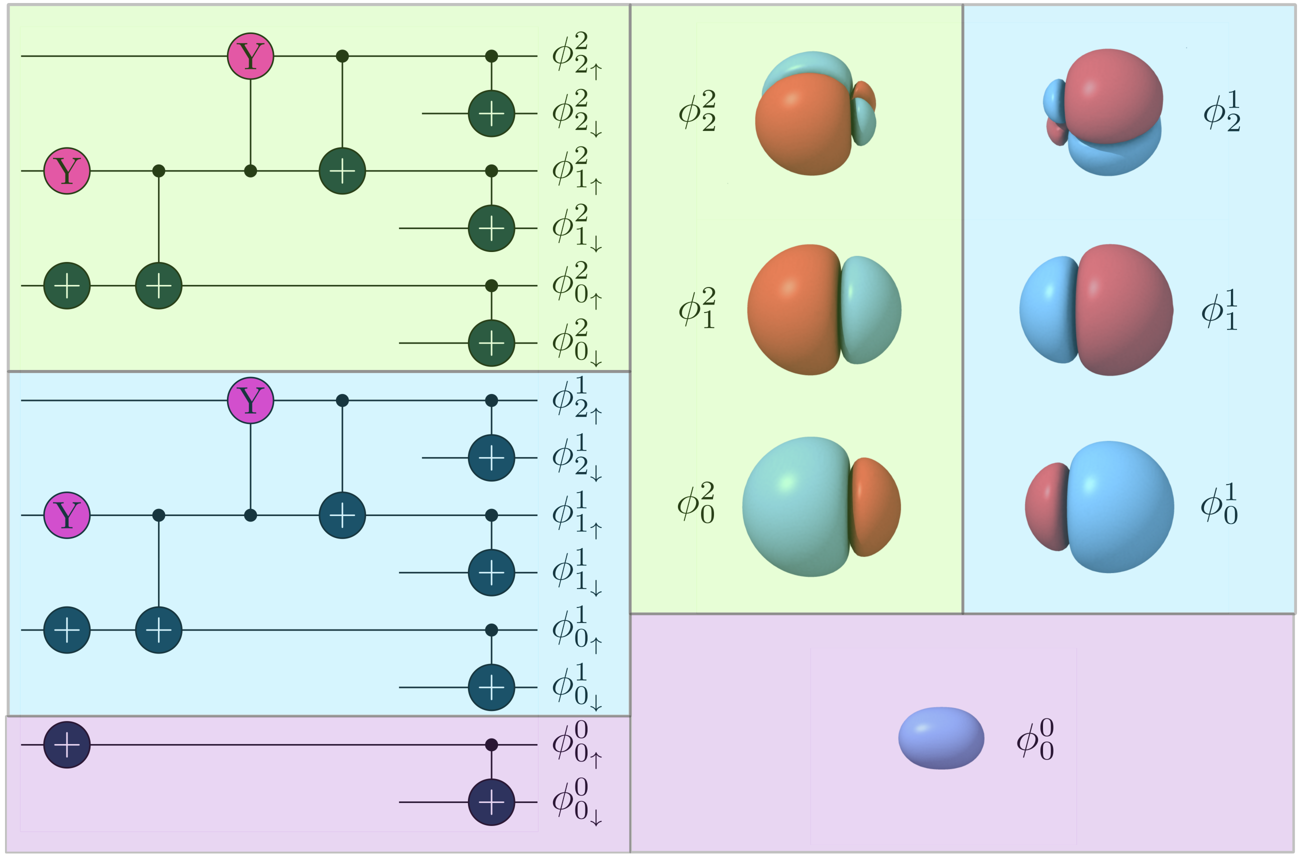

| Molecule($N_e$,$N_q$) | $N_{param}$ | $N_{cnot}$ | Depth |
|---|---|---|---|
| $H_2$(2,4) | 1 | 3 | 3 |
| LiH(2,10) | 4 | 15 | 18 |
| $BeH_2$(4,8) | 2 | 6 | 3 |
| $BeH_2$(6,14) | 4 | 15 | 7 |
| $BH_3$(6,12) | 3 | 9 | 3 |
| $N_2$(6,12) | 3 | 9 | 3 |
| $C_2H_4$(12,24) | 6 | 18 | 3 |
| $H_2O_2$(14,28) | 7 | 21 | 3 |
| $C_2H_6$(14,28) | 7 | 21 | 3 |
| $C_2H_6$(2,12) | 5 | 19 | 23 |
| $C_2H_6$(14,84) | 35 | 133 | 23 |

JSK, A. Aspuru-Guzik, Arxiv:2105.03836, 2021

# Development Example: Separable Pair Approximations

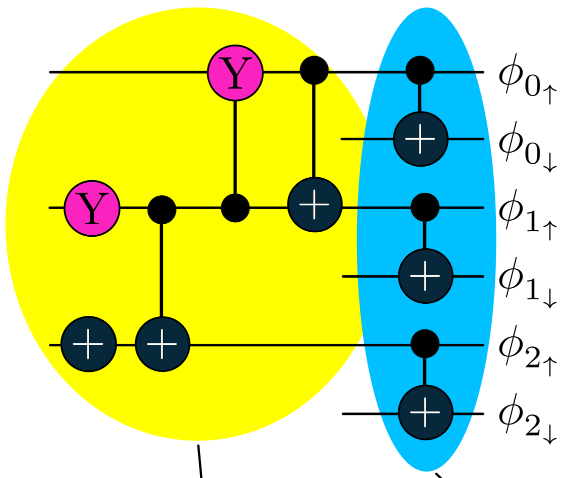



High level circuit design through physical principles




JSK, A. Aspuru-Guzik, Arxiv:2105.03836, 2021

# Possible Extensions




transfer to Jordan-Wigner

wavefunction preparation in paired sector

"Pairing models", "Hardcore-Boson", "Seniority-Zero"

access to similar ideas:

Elfving *et.al*, PRA, 2021

Khamoshi, Evangelista, Scuseria, QST, 2020

combine with other approaches:

Anselmetti, arXiv:2104.05695, 2021

```
class JordanWigner(EncodingBase):
    ....
    def hcb_to_me(self, *args, **kwargs):
        U = QCircuit()
        for i in range(self.n_orbitals):
            U += X(target=self.down(i), control=self.up(i))
        return U
```

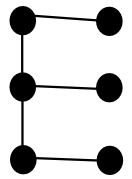
$$U^{\mathrm{X}}_{\mathrm{HCB}} = U^{\mathrm{X}}_{\mathrm{JW}} U^{\mathrm{JW}}_{\mathrm{HCB}}$$

$\mathrm{X} \in \{\text{Bravyi-Kitaev}, \dots\}$

quasi-local codes: Chien & Whitfield, arXiv:2009.11860

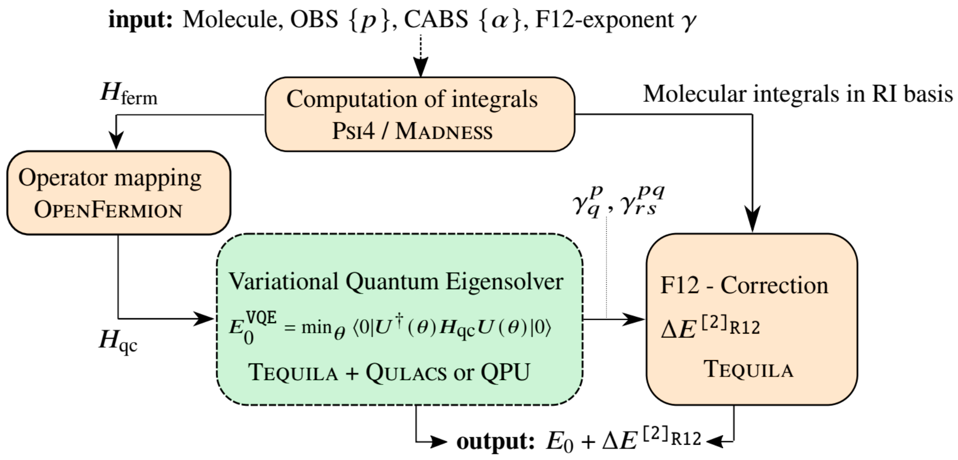
BKSF: Setia, Bravyi, Mezzacapo, Whitfield, PRR 2019

explore quit connectivity



# Recent Developments

Explicit Correlation



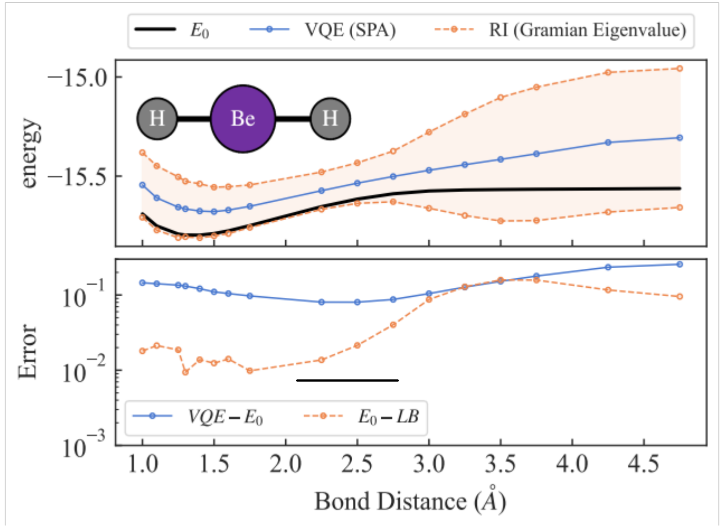

P. Schleich, JSK, A. Aspuru-Guzik, Arxiv:2110.06812, 2021

See also: Master thesis from Philipp Schleich (detailed introduction)

Robustness Intervals: Weber *et.al*, arXiv:2110.09793

| | SDP | Gramian | |
|---|---|---|---|
| | Expectation $\langle A\rangle_\sigma$ | Expectation $\langle A\rangle_\sigma$ | Eigenvalue $\lambda$ |
| Lower Bound | $(1-2\epsilon)\langle A\rangle_\rho - 2\sqrt{\epsilon(1-\epsilon)(1-\langle A\rangle_\rho^2)}$ | $(1-2\epsilon)\langle A\rangle_\rho - 2\sqrt{\epsilon(1-\epsilon)}\Delta A_\rho + \frac{\epsilon\langle A^2\rangle_\rho}{\langle A\rangle_\rho}$ | $\langle A\rangle_\rho - \Delta A_\rho\sqrt{\frac{\epsilon}{1-\epsilon}}$ |
| Upper Bound | $(1-2\epsilon)\langle A\rangle_\rho + 2\sqrt{\epsilon(1-\epsilon)(1-\langle A\rangle_\rho^2)}$ | — | $\langle A\rangle_\rho + \Delta A_\rho\sqrt{\frac{\epsilon}{1-\epsilon}}$ |
| Assumptions | $-\mathbb{1} \le A \le \mathbb{1}$ | $A \ge 0$ | $\sigma = \vert\psi\rangle\langle\psi\vert \;\wedge\; A\vert\psi\rangle = \lambda\vert\psi\rangle$ |

TABLE I. Overview of bounds for the expectation values and eigenvalues of an Hermitian operator $A$ under a target state $\sigma$, with $\rho$ an approximation of $\sigma$. For the eigenvalue bound, $\sigma = |\psi\rangle\langle\psi|$ is the density operator corresponding to the eigenstate $|\psi\rangle$ with eigenvalue $\lambda = \langle\psi|A|\psi\rangle$. We remark that the SDP lower and upper bounds are valid for fidelities with $\mathcal{F}(\rho,\sigma) \ge 1-\epsilon$ for $\epsilon \ge 0$ such that $\epsilon \le \frac{1}{2}(1+\langle A\rangle_\rho)$ and $\epsilon \le \frac{1}{2}(1-\langle A\rangle_\rho)$, respectively. The Gramian lower bound for expectation values is valid for $\epsilon \ge 0$ with $\sqrt{1-\epsilon/\epsilon} \ge \Delta A_\rho/\langle A\rangle_\rho$.




gradients, orbitals, circuits: All used in black-box fashion

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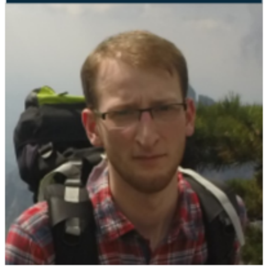

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