

many body Schrodinger equation

(time-independent)

All of these approximations leave us with:

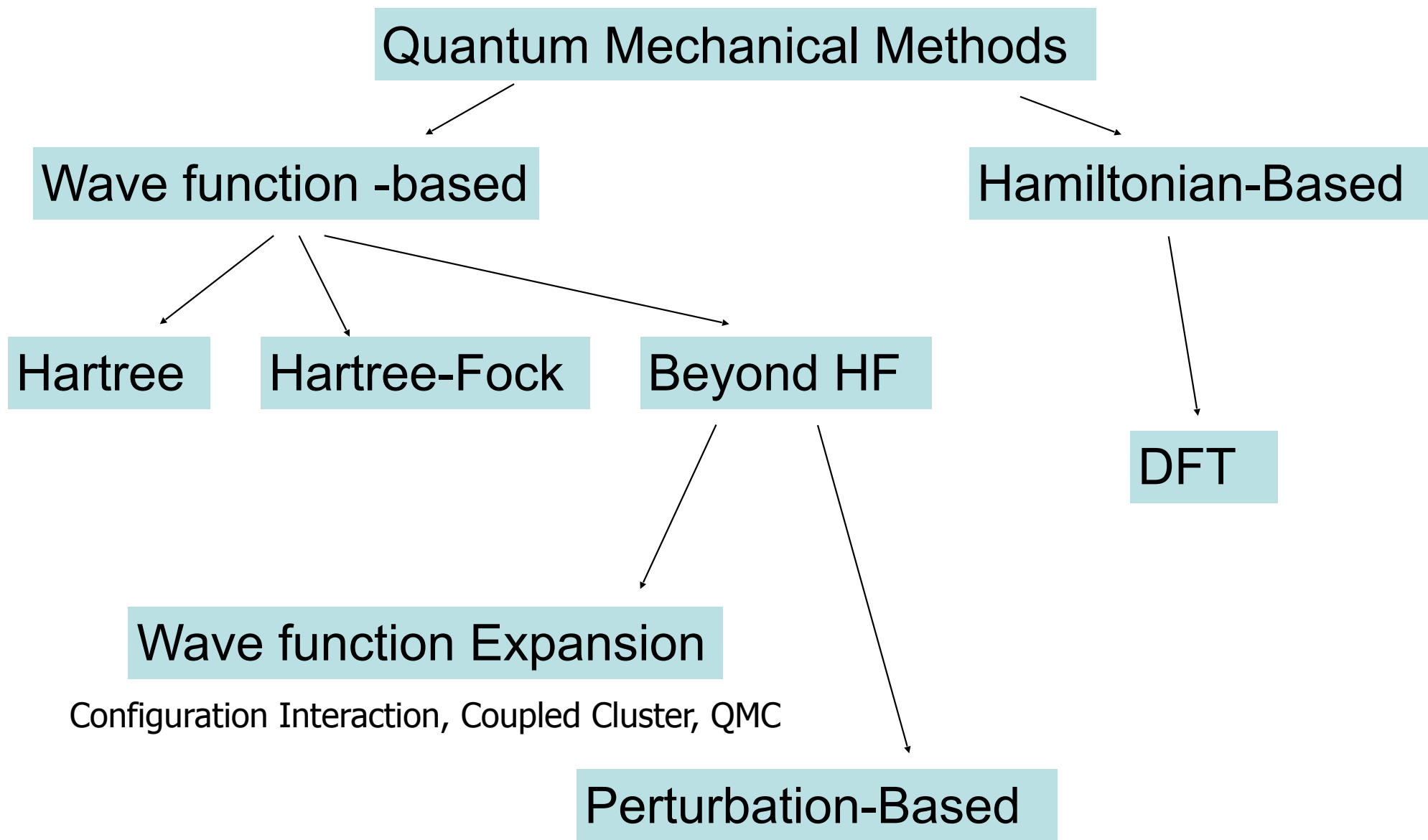
$$H\psi(r_1, \dots, r_n) = E\psi(r_1, \dots, r_n)$$

$$\hat{H} = \underbrace{-\frac{1}{2}\nabla^2 - \sum \frac{Z_n}{r_{e-n}}}_{\text{Non-interacting part}} + \underbrace{\sum \frac{1}{r_{e-e}}}_{\text{Contains an Electron-Electron Distance!}}$$

This part is “easy”. If we only had these two terms, the electrons would be non-interacting and the solution for the wave function actually would be separable.

In reality, the electrons do interact with each other. This existence of this term makes the actual solution not separable in fact.

methods

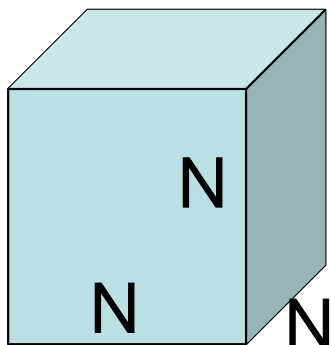


Hamiltonian based methods

wave function vs. electron density

- We've talked about the Hartree, Hartree-Fock, and post-HF approaches. We've also seen that we get poor scaling when we want to include any correlation effects at all.
- An underlying issue here is that, no matter how you slice it, the wave function Ψ is a beast of an entity to have to deal with.
- For example, consider that we have n electrons populating a 3D space. Let's divide 3D space into $N \times N \times N = 2 \times 2 \times 2$ grid points. To reconstruct Ψ , how many points must we keep track of?

$$\Psi = \Psi(r_1, \dots, r_n) \quad \# \text{ of points} = N^{3n}$$



$n = \#$ electrons	Ψ (N^{3n})	ρ (N^3)
1	8	8
10	10^9	8
100	10^{90}	8
1000	10^{900}	8

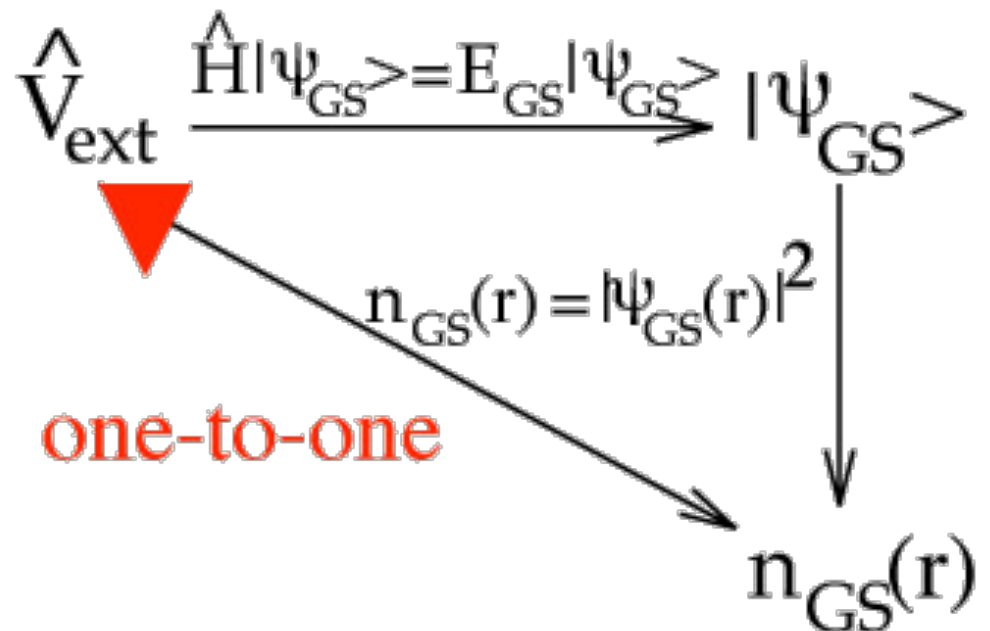
- The electron density seems to be a more manageable quantity. **Wouldn't it be nice if we could reformulate our problem in terms of the density, rather than the wave function?**

Hohenberg-Kohn I

- As it turns out, we can - and this is the basis for DFT.
- In order to reformulate our problem in terms of the electronic density, we must first establish a few ground rules
- These are, namely, the two Hohenberg-Kohn theorems and the Kohn-Sham formalism

HOHENBERG-KOHN I

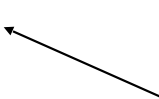
- The external potential corresponds to a unique ground state electron density.
- A given ground state electron density corresponds to a unique external potential
- In particular, there is a one to one correspondence between the external potential and the ground state electron density



Hohenberg-Kohn II

There exists a universal functional of the density $F[\rho(r)]$ such that the ground state energy E

$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})]$$

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is minimized at the true ground state density.

Note how **very useful** this is. We now have a variational theorem to obtain the ground state density (and, correspondingly, the energy)

By the way, what is a “functional”?

A functional is a mapping from a function (the electron density) to a number (the ground state energy).

The equation that we need to solve comes from taking a functional derivative

$$\frac{\delta}{\delta\rho} \left(E - \mu \int \rho(r)dr \right) = V_{ext} + \frac{\delta F}{\delta\rho} - \mu = 0$$

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Note that a Lagrange multiplier has showed up. The constraint that we are accommodating is:

$$n = \int \rho(\mathbf{r}) d\mathbf{r}$$

Hohenberg-Kohn II

But, back to the functional form of the Hohenberg-Kohn expression, which we will use to evaluate the energy.

$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})]$$

Aha - we have gone from the $3n$ dimensional integrals to the 3 dimensional integrals.

i.e., previously, we had to deal with:

$$E = \int \Psi^* (V_{ext} + T + V_{int}) \Psi d^{3n}r$$

In principle - if you tell me the ground state electron density, I can plug into this integral expression and give you the GS energy.

But wait ... what is the form of the universal functional F ? We only said that it exists; we did not specify what it is.

This is, in fact, the origin of the ubiquitous statement that “In principle, DFT is exact. In practice, we must approximate.”

What might $F[\rho(\mathbf{r})]$ look like?

From simple inspection:

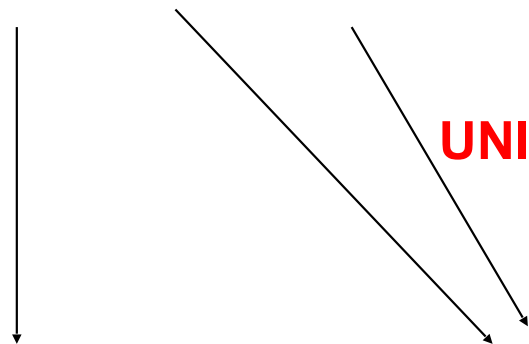
$$E = \int \Psi^* (V_{ext} + T + V_{int}) \Psi d^{3n}r$$


Diagram illustrating the mapping of terms from the energy equation to the functional equation:

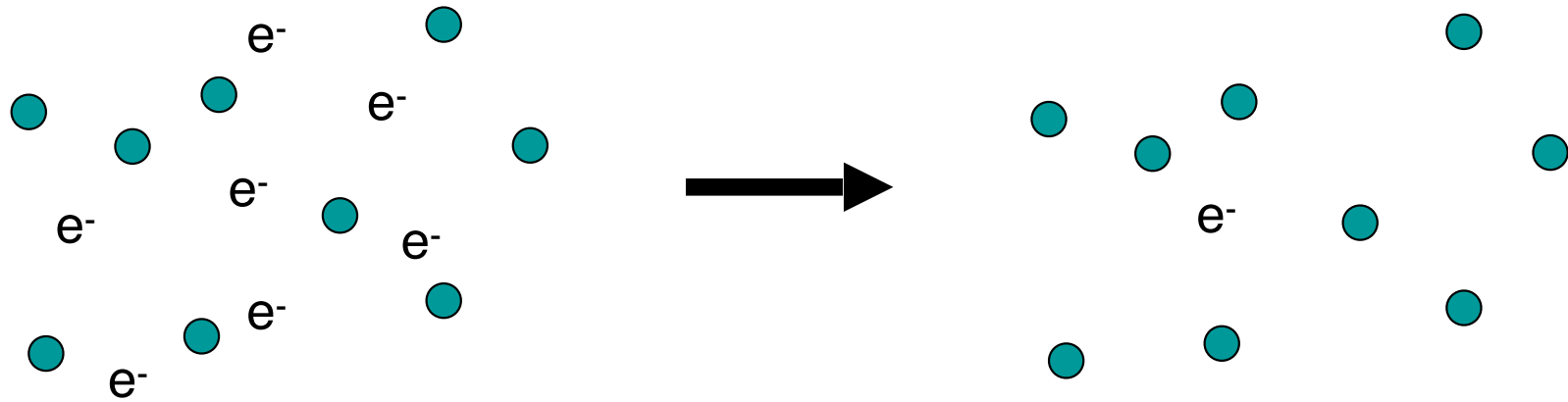
- An arrow points from V_{ext} in the first equation to $V_{ext}(\mathbf{r})$ in the second equation.
- An arrow points from T in the first equation to $F[\rho(\mathbf{r})]$ in the second equation.
- An arrow points from V_{int} in the first equation to $F[\rho(\mathbf{r})]$ in the second equation.

$$E[\rho(\mathbf{r})] = \int V_{ext}(\mathbf{r})\rho(\mathbf{r})d\mathbf{r} + F[\rho(\mathbf{r})]$$

Naively, we might expect the functional to contain terms that resemble the kinetic energy of the electrons and the coulomb interaction of the electrons

Density Functional Theory

- Completely rigorous approach to any interacting problem in which we can map, exactly, the interacting problem to a non-interacting one.



$$\hat{H} = \underbrace{\frac{1}{2} \sum_{j=1}^N \sum_{i=1}^N \frac{Z_i Z_j e^2}{|R_i - R_j|}}_{V_{ext}(r_j)} - \underbrace{\sum_{j=1}^N \sum_{i=1}^n \frac{Z_j e^2}{|r_i - R_j|}}_T + \underbrace{\sum_{j=1}^n \left(-\frac{\hbar^2}{2m} \right) \nabla_{r_j}^2}_{V_{int}} + \underbrace{\frac{1}{2} \sum_{j=1}^n \sum_{i=1}^n \frac{e^2}{|r_i - r_j|}}_{V_{int}}$$

interacting particles in a real external potential

$$\hat{H} = \left(-\frac{\hbar^2}{2m} \right) \nabla_r^2 + V_{eff}(r)$$

Kohn-Sham system: a set of non-interacting electrons (with the same density as the interacting system) in some effective potential

Kohn-Sham Approach

Kohn and Sham said:

$$F[\rho(\mathbf{r})] = E_{KE}[\rho(\mathbf{r})] + E_H[\rho(\mathbf{r})] + E_{XC}[\rho(\mathbf{r})]$$

Where we have a separation of kinetic, Coulomb, and exchange/correlation terms.

Importantly, the kinetic part is defined as the kinetic energy of the system of **non-interacting** electrons at the same density.

The Coulomb term is simply the Hartree electrostatic energy - namely, a classical interaction between two charges summed over all possible pairwise interactions.

The equation above, in a sense, acts to define the last term, the exchange-correlation part, as simply everything else that should be there to make this approximation to F as accurate as possible.

Ingredients to Density Functional Theory

- Ingredients:
 - Note that what differs from one electronic system to another is the external potential of the ions
 - Hohenberg-Kohn I: one to one correspondence between the external potential and a ground state density
 - Hohenberg-Kohn II: Existence of a universal functional such that the ground state energy is minimized at the true ground state density

$$E = \min_{\rho} \left\{ \int V_{\text{ext}}(\mathbf{r}) \rho(\mathbf{r}) d\mathbf{r} + F[\rho(\mathbf{r})] \right\}$$

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- The universality is important. This functional is exactly the same for any electron problem. If I evaluate F for a given trial orbital, it will always be the same for that orbital - regardless of the system of particles.
- Kohn-Sham: a way to approximate the functional F

Euler-Lagrange System

The Hohenberg-Kohn theorems give us a variational statement about the ground state density:

$$\frac{\delta}{\delta \rho} \left(E - \mu \int \rho(r) dr \right) \Rightarrow \frac{\delta F}{\delta \rho} + V_{ext} = \mu$$

“the exact density makes the functional derivative of F exactly equal to the negative of the external potential (to within a constant)”

If we knew how to evaluate F , we could solve all Coulombic problems exactly.

However, we do not know how to do this. We must, instead, approximate this functional. This is where Kohn-Sham comes in.

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Kohn-Sham Approach

The next step to solving for the energy in the Kohn-Sham approach is to introduce a set of one-electron orthonormal orbitals.

$$\rho(\mathbf{r}) = \sum_{i=1}^N |\varphi_i(\mathbf{r})|^2$$

Now the variational condition can be applied, and one obtains the one-electron Kohn-Sham equations.

$$\left\{ -\frac{\nabla_1^2}{2} - \left(\sum_{A=1}^M \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} d\mathbf{r}_2 + V_{xc}[\rho(\mathbf{r}_1)] \right\} \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1)$$

Where V_{xc} is the exchange correlation functional, related to the xc energy as:

$$V_{xc}[\mathbf{r}] = \left(\frac{\delta E_{xc}[\rho(\mathbf{r})]}{\delta \rho(\mathbf{r})} \right)$$

Comparison with Hartree-Fock

$$\left\{ -\frac{\nabla_1^A}{2} - \left(\sum_{A=1}^M \frac{Z_A}{r_{1A}} \right) + \int \frac{\rho(\mathbf{r}_2)}{r_{12}} + V_{XC}[\mathbf{r}_1] \right\} \varphi_i(\mathbf{r}_1) = \varepsilon_i \varphi_i(\mathbf{r}_1)$$

Naturally, you're remembering the Hartree-Fock equations and realizing that this equation is in fact quite similar:

$$\left[-\frac{\hbar^2}{2m_e} \nabla_{\mathbf{r}_i}^2 + V_{ion}(\mathbf{r}_i) + e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_j \right\rangle \right] \varphi_i(\mathbf{r}_i) - e^2 \sum_{j \neq i} \left\langle \varphi_j \left| \frac{1}{|\mathbf{r}_i - \mathbf{r}_j|} \right| \varphi_i \right\rangle \varphi_j(\mathbf{r}_i) = \varepsilon_i \varphi_i(\mathbf{r}_i)$$

So, just as with Hartree-Fock, the approach to solving the Kohn-Sham equations is a self-consistent approach.

That is, an initial guess of the density is fed into the equation, from which a set of orbitals can be derived. These orbitals lead to an improved value for the density, which is then taken in the next iteration to recompute better orbitals. And so on.

Kohn-Sham System

To solve the Kohn-Sham equations, a number of different methods exist.

These tend to differ first and foremost in the choice of basis set for expanding the Kohn-Sham orbitals.

As in Hartree-Fock, for molecular systems a typical choice can be some type of atom-centered basis such as sums of Gaussians.

In extended (e.g., solid, liquid) systems, plane waves are a much more suitable choice of basis.

One important difference between DFT and Hartree-Fock, in general, is that the Kohn-Sham orbitals used in DFT are a set of non-interacting orbitals designed to give the correct density and **have no physical meaning beyond that.**

This is in contrast to the orbitals in Hartree-Fock theory, which directly represent electrons and are designed to give the correct wave function as opposed to just the density.

Electronic minimization: Reaching the groundstate

Direct minimization of the DFT functional (*e.g.* Car-Parrinello): start with a set of trial orbitals (random numbers) and minimize the energy by propagating the orbitals along the gradient:

$$\text{Gradient: } F_n(\mathbf{r}) = \left(-\frac{\hbar^2}{2m_e} \nabla^2 + V^{\text{eff}}(\mathbf{r}, \{\psi_n(\mathbf{r}')\}) - \epsilon_n \right) \psi_n(\mathbf{r})$$

The Self-Consistency-Cycle: start with a trial density, construct the corresponding Hamiltonian. Solve it to obtain a set of orbitals:

$$\left(-\frac{\hbar^2}{2m_e} \nabla^2 + V^{\text{eff}}(\mathbf{r}, \{\rho(\mathbf{r}')\}) \right) \psi_n(\mathbf{r}) = \epsilon_n \psi_n(\mathbf{r}) \quad n = 1, \dots, N_e/2$$

These orbitals define a new density, that defines a new Hamiltonian, ...
iterate to self-consistency

The Self-Consistency-Cycle (cont.)

Two sub-problems:

- Optimization of $\{\psi_n\}$
Iterative Diagonalization
e.g. RMM-DIIS or Blocked Davidson
- Construction of ρ_{in}
Density Mixing
e.g. Broyden mixer

