Separate the full Hamiltonian into one- and two-body parts

H2 molecule, r = 1.4 Bohr minimal basis

The full Hamiltonian:

$$H = \left(-\frac{1}{2}\nabla_1^2 - \sum_A \frac{Z_A}{r_{1A}} \right) + \left(-\frac{1}{2}\nabla_2^2 - \sum_A \frac{Z_A}{r_{2A}} \right) + \frac{1}{r_{12}}$$

$$= h(1) + h(2) + \frac{1}{r_{12}}$$

$$= \mathcal{O}_1 + \mathcal{O}_2$$

Connect this with the model Hamiltonian:

$$H_{\text{eff}} = E_0 + \sum_{ij} t_{ij} \left(c_i^\dagger c_j + \text{ h.c. } \right) + \sum_{ijkl} V_{ijkl} c_i^\dagger c_j^\dagger c_k c_l$$

Compute the 1e integrals

For minimal basis H2, one can show that for the matrix element of $\mathcal{O}_1$

$$\langle \Psi_0 | \mathcal{O}_1 | \Psi_0 \rangle = \langle 1|h|1\rangle + \langle 2|h|2\rangle$$

1e-integrals

$$\langle i|h|j\rangle = \langle \chi_i|h|\chi_j\rangle = \int \mathrm{d}\mathbf{x}\chi_i^*(\mathbf{x})h(\mathbf{x})\chi_j(\mathbf{x})$$

In terms of spatial MO:

$$\langle \Psi_0 \,|\mathcal{O}_1|\, \Psi_0\rangle = 2(1|h|1)$$

Compute the 1e integrals in MO basis

```python
# compute the 1e integrals
ham_1e_kin = pyscf.gto.getints("int1e_kin_sph", mol._atm, mol._bas, mol._env)
ham_1e_nuc = pyscf.gto.getints("int1e_nuc_sph", mol._atm, mol._bas, mol._env)

ham_1e = ham_1e_kin + ham_1e_nuc

# transform into MO basis
ham_1e_mo = np.einsum('kl,ki,lj', ham_1e, mf.mo_coeff, mf.mo_coeff)
print('direct 1e integrals in MO:\n', ham_1e_mo)
```

✓ 0.3s Python

```
direct 1e integrals in MO:
 [[-1.18552106e+00 -1.11022302e-16]
 [ 0.00000000e+00 -5.73440850e-01]]
```

Compute the 1e integrals in localized orbitals

```
# transform into the localized basis
ham_1e_lo = np.einsum('kl,ki,lj', ham_1e, a, a)
print('direct 1e integrals in LO:\n', ham_1e_lo)
```

✓ 0.9s Python

```
direct 1e integrals in LO:
 [[-0.87948095 -0.3060401 ]
 [-0.3060401  -0.87948095]]
```

Reference: the t derived from DMD:
-0.289(3)

You can compare them with the downfolded 1body tight-binding model

```
TB Ham:
 [[-0.11020441 -0.50912646]
 [-0.50912646 -0.11020441]]
```

The bare Coulomb interaction

$$\langle \Psi_0 | \mathcal{O}_2 | \Psi_0 \rangle = \langle 12|12\rangle - \langle 12|21\rangle$$

2e-integrals

$$\langle ij|kl\rangle = \langle \chi_i \chi_j | \chi_k \chi_l \rangle = \int \mathrm{d}\mathbf{x}_1 \mathrm{d}\mathbf{x}_2 \chi_i^*(\mathbf{x}_1) \chi_j^*(\mathbf{x}_2) r_{12}^{-1} \chi_k(\mathbf{x}_1) \chi_l(\mathbf{x}_2)$$

Pyscf convention: (the chemists' notation, in terms of spatial orbitals)

$$(ij \mid kl) = \int \mathrm{d}\mathbf{x}_1 \ \mathrm{d}\mathbf{x}_2 \phi_i^* (\mathbf{x}_1) \phi_j (\mathbf{x}_1) r_{12}^{-1} \phi_k^* (\mathbf{x}_2) \phi_l (\mathbf{x}_2)$$

Coulomb integrals: $(ii \mid jj)$

Exchange integrals: $(ij \mid ji)$

Compute the 2e integrals in MO basis

```python
# compute the 2e integrals
int_2e_ao = pyscf.gto.getints("int2e_sph", mol._atm, mol._bas, mol._env)
int_2e_mo = np.einsum('klmn,ka,lb,mc,nd->abcd', int_2e_ao, mf.mo_coeff, mf.
mo_coeff, mf.mo_coeff, mf.mo_coeff)

print('direct 2e integrals in MO:\n',int_2e_mo)
```

✓ 0.6s Python

```
direct 2e integrals in MO:
 [[[[ 5.66190189e-01 -5.55111512e-17]
   [-5.55111512e-17  5.56277523e-01]]

  [[-2.77555756e-17  1.40192148e-01]
   [ 1.40192148e-01 -1.11022302e-16]]]


 [[[-1.38777878e-16  1.40192148e-01]
   [ 1.40192148e-01 -5.55111512e-16]]

  [[ 5.56277523e-01 -3.33066907e-16]
   [ 0.00000000e+00  5.85863852e-01]]]]
```

Check that only terms such as 0,0,0,0, 0,0,1,1 or 0,1,1,0 are nonzero

Compute the 2e integrals in localized orbitals

```
int_2e_lo = np.einsum('klmn,ka,lb,mc,nd->abcd', int_2e_ao, a, a, a, a)

print('direct 2e integrals in LO:\n',int_2e_lo)
```

✓ 0.2s Python

```
direct 2e integrals in LO:
 [[[[ 0.70634442 -0.00491842]
    [-0.00491842  0.42596012]]

   [[-0.00491842  0.00987475]
    [ 0.00987475 -0.00491842]]]



 [[[-0.00491842  0.00987475]
    [ 0.00987475 -0.00491842]]

   [[ 0.42596012 -0.00491842]
    [-0.00491842  0.70634442]]]]
```

Reference: the Hubbard U derived from DMD: 0.19(2)

More: compute the 1e and 2e contribution to the total energy…