Exercise Ex4

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Please use this template to submit your answers.
If you had to modify code from the notebook, please include the modified code in your submission either as screenshot or in a

```
\begin{lstlisting}[language=Python]
\end{lstlisting}
```

environment.
You only need to include the code cells that you modified.
Note, that references to other parts of the documents aren't resolved in this template and will show as `??`. Check the text of the exercises on website for the reference

Exercise 1
Define S_{ij} using Dirac notation.

$$S_{ij} = \langle i|j\rangle = \langle \phi_i|\phi_j\rangle$$

Exercise 2
For an orthonormal basis, what does the overlap integral array, `S`, look like?

For an orthonormal basis, $S_{ij} = \delta_{ij}$. `S` is the identity matrix. It has the dimension equals to the size of our basis set.

Exercise 3
Use `B` and `B_dagger` and the matrix rules above to calculate the matrix `S`.

```
S = B_dagger.dot(B)
```

Exercise 4
Describe how the notation of the `np.einsum` command correlates to the implicit summation formula written above.

```
S=numpy.einsum('ip,iq->pq',B.conj(),B)
```

It means that we indicate to numpy a repeated index i on which we will make the implicit summation. Indeed we will sum on i tensor B^*_{ip} with tensor B_{iq} and reorganize the result as a new tensor S_{pq}. This corresponds to $\sum_i B^*_{ip} B_{iq} = S_{pq}$ which is exactly the overlap matrix.

Exercise 5
Use the function `np.einsum()` to calculate the matrix `S`, and confirm that your answer is the same as above.

```
S = np.einsum('ip,iq->pq',B.conj(),B) #<your formula here>
print(F'S from Einstein notation:\n{S}')
```

```
S from Einstein notation:  [[1.  0.]  [0.  1.]]
```

Exercise 6
Propose a different orthonormal basis, modify `phi1` and `phi2`, and verify that `S` still has the same form. There are infinitely many choices. It isn't complex... or *is* it?!

```
# two orthonormal vectors
phi1 = np.array([np.cos(.5), np.sin(.5)]) #insert here
phi2 = np.array([np.sin(.5), -np.cos(.5)]) #insert here

# construct the overlap matrix from matrix of basis vectors
vector_length = phi1.size #length of the vector space
phi1_column = phi1.reshape(vector_length,1) #this makes phi a
    column vector
phi2_column = phi2.reshape(vector_length,1)

# put together (concatenate) the vectors into the matrix B
B = np.concatenate((phi1_column,phi2_column),axis=1)
print(F'The matrix B:\n{B}')

B_dagger = B.conj().T
print(F'The matrix B^\\dagger:\n{B_dagger}')

# calculate S from matrix of basis vectors
S = np.einsum('ip,iq->pq',B.conj(),B)
print(F'S from Einstein notation:\n{S}')
```

```
The matrix B: [[ 0.87758256 0.47942554] [ 0.47942554 -0.87758256]]
The matrix B^†:  [[ 0.87758256 0.47942554] [ 0.47942554 -0.87758256]]
S from Einstein notation:  [[1.  0.]  [0.  1.]]
```

Exercise 7
How many electrons are there in total in H_2O? How many occupied molecular orbitals would you expect?

There are 10 electrons in H_2O molecule. They are occupied orbitals 5 orbitals. We have one first orbital for the core electrons, which are paired, and are from O. Then O has two unpaired electrons which will form each a covalent bond with each electron from H atoms, leading to 1 orbital each. Finally, O has two lone pairs for which we allocate to each an orbital.

Exercise 8
Explain the shape (number of rows and columns) of `S` in terms of the AO basis set we chose.

```
# Construct a molecular integrals object
mints = psi4.core.MintsHelper(wfn.basisset())

# Overlap matrix as a psi4 Matrix object
S_matrix = mints.ao_overlap()

# Overlap matrix converted into an ndarray
S = np.asarray(S_matrix)

print(F'Shape of S is {S.shape}')
```

```
Shape of S is (7, 7)
```

Since we have 7 basis fonctions, we need to calculate the overlap S_{ij} for all pairs $\{i, j\} \in \{1, ..., 7\}^2$. Leading to a matrix of dimension 7×7. STO-3G gives 5 basis functions for O ($1s^2 2s^2 2p^4$, one basis functions for each orbital) and 1 per H atoms ($1s^2$). Therefore :

$$S = \begin{pmatrix} \langle\phi_1|\phi_1\rangle & \langle\phi_1|\phi_2\rangle & \langle\phi_1|\phi_3\rangle & \cdots \\ \langle\phi_2|\phi_1\rangle & \langle\phi_2|\phi_2\rangle & \langle\phi_2|\phi_3\rangle & \cdots \\ \langle\phi_3|\phi_1\rangle & \langle\phi_3|\phi_2\rangle & \langle\phi_3|\phi_3\rangle & \cdots \\ \vdots & \vdots & \vdots & \ddots \\ & & & \langle\phi_7|\phi_7\rangle \end{pmatrix}$$

Exercise 9
Based on your observations of `S` in the AO basis, answer the following questions

1. What do the diagonal elements of `S` indicate?
2. What do the off-diagonal elements of `S` indicate?

3. Does the Gaussian atomic orbital basis set form an orthonormal basis?

1. The diagonal terms are equal to 1, the basis sets is normalized.
2. Most of the terms are 0 but some terms are of order 10^{-1} and 10^{-2} indicating that the overlap between two different atomic orbitals is not always 0 and that not all states are orthogonal.
3. The Gaussian atomic orbital basis set does not form a complete orthonormal basis set due to significant overlap between some orbitals. `S` will have to be considered for further calculations.

Exercise 10
Does the result of your extra evaluation agree with what you determined previously?

```
isBasisOrthonormal(S)
```

```
  Q:(T/F) The AO basis is orthonormal?  A: False
False
```

This confirms the fact that the gaussian atomic orbital basis set does not form a complete ortho-normal basis set.

Exercise 11
Use the function `np.linalg.inv()` to calculate the inverse of `S`, and the function `splinalg.sqrtm()` to take its (matrix) square root. Execute the code below and examine the matrix `A`.

```
S_inverse = np.linalg.inv(S)

A = splinalg.sqrtm(S_inverse)

peak(A)
```

```
  Here is a peak at the first 4 x 4 elements of the matrix:
[[ 1.02363458 -0.13685468 -0.00748725 0.  ]
[-0.13685468 1.15786316 0.07216005 0.  ]
[-0.00748725 0.07216005 1.03830504 0.  ]
[ 0.  0.  0.  1.  ]]
```

The matrix A shows that the gaussian atomic orbital basis set does not form a complete ortho-normal basis set since it would have been the identity if this was the case. Indeed if $S = \mathbb{I}$ then $A = \mathbb{I}$

Exercise 12
What do you observe about the elements of `A`? Is the matrix real or complex? Is the matrix symmetric or not?

Elements of A alsmost all non-zero and are positive and negative-valued. A inherits its properties from the ones of The overlap matrix S which is hermitian ($S = S^\dagger$). Now $A = S^{-1/2} = \sum_{i=1}^{7} \lambda_i^{-1/2} |\lambda_i\rangle\langle\lambda_i|$, where $\{|\lambda_i\rangle\}$ are the eigenvalues of S, so we know that A is hermitian and therefore symmetric as shown in the figure. In our case, A is symmetric and real.

```
array([[ 1.02363458e+00, -1.36854677e-01, -7.48725467e-03,
         0.00000000e+00, -1.08457284e-18,  1.90278847e-02,
         1.90278847e-02],
       [-1.36854677e-01,  1.15786316e+00,  7.21600498e-02,
         0.00000000e+00,  3.64651649e-17, -2.22332521e-01,
        -2.22332521e-01],
       [-7.48725467e-03,  7.21600498e-02,  1.03830504e+00,
         0.00000000e+00, -3.75981753e-17, -1.18462545e-01,
        -1.18462545e-01],
       [ 0.00000000e+00,  0.00000000e+00,  0.00000000e+00,
         1.00000000e+00,  0.00000000e+00,  0.00000000e+00,
         0.00000000e+00],
       [-3.45874404e-19,  5.02534544e-17, -4.01081341e-17,
         0.00000000e+00,  1.07331473e+00,  1.75758279e-01,
        -1.75758279e-01],
       [ 1.90278847e-02, -2.22332521e-01, -1.18462545e-01,
         0.00000000e+00,  1.75758279e-01,  1.12972338e+00,
        -6.25974978e-02],
       [ 1.90278847e-02, -2.22332521e-01, -1.18462545e-01,
         0.00000000e+00, -1.75758279e-01, -6.25974978e-02,
         1.12972338e+00]])
```

Figure 1: Matrix A

Exercise 13
Use the orthogonalization matrix `A` to transform the overlap matrix, `S`. Check the transformed overlap matrix, `S_p`, to make sure it represents an orthonormal basis.

```
# Transform S with A and assign the result to S_p

S_p = A.dot(S.dot(A)) #<your equation here>

isBasisOrthonormal(S_p)
```

```
Q:(T/F) The AO basis is orthonormal?  A: True
```
`True` S' now represents an orthonormal basis.

Exercise 14
The product A S A does not take the complex conjugate transpose of A. What conditions (properties of A) make that ok?

A is hermitian and real, making it a symmetric matrix, indeed we have : $A^\dagger = A$.

Exercise 15
Based on the definition of C', propose a definition of C in terms of A and C'. Justify your equation.

$$C' = A^{-1}C$$
$$AC' = AA^{-1}C$$
$$C = AC' \quad \text{where we used that } A \text{ is invertible such that } A^{-1}A = \mathbb{I}$$

Exercise 16
In the cell below, use the core Hamiltonian matrix as your initial guess for the Fock matrix. Transform it with the same A matrix you used above. To calculate the eigenvalues, `vals`, and eigenvectors, `vecs`, of matrix `M` using `vals, vecs = np.linalg.eigh(M)`.

```
# Guess for the Fock matrix
F = H # Replace

# Transformed Fock matrix
F_p =  A.dot(F.dot(A)) # Replace

# Diagonalize F_p for eigenvalues & eigenvectors with NumPy
e, C_p =  np.linalg.eigh(F_p) # Replace
```

Exercise 17
Display, i.e., `print`, the coefficent matrix and confirm it the correct size

```
print(C_p)
print("The size of the coefficient matrix is:",C_p.shape)
```

```
[[-9.93397459e-01  1.06813566e-01 -1.35307498e-16 -4.17010426e-02
   1.76149298e-15 -3.65697236e-03  1.33010607e-16]
 [-1.14180122e-01 -9.13965568e-01  1.27788258e-15  3.67704764e-01
  -1.55859911e-14  1.28152437e-01 -2.37455910e-15]
 [-7.66151195e-04 -3.68538378e-01 -2.99255600e-15 -9.28905590e-01
   4.00351377e-14  3.62392157e-02 -1.59671447e-15]
 [ 0.00000000e+00 -3.33066907e-16  3.57353036e-16 -4.30211422e-14
  -1.00000000e+00 -3.33066907e-16  5.55111512e-17]
 [ 2.31531739e-18  4.71826794e-17  9.98991226e-01 -3.20984454e-15
   4.77769914e-16 -1.24429917e-15 -4.49058022e-02]
 [-7.86768545e-03 -9.33736227e-02 -3.17531973e-02  9.71167846e-03
  -3.92055707e-16 -7.00803217e-01 -7.06393470e-01]
 [-7.86768545e-03 -9.33736227e-02  3.17531973e-02  9.71167846e-03
   2.74078108e-16 -7.00803217e-01  7.06393470e-01]]
The size of the coefficient matrix is: (7, 7)
```

Exercise 18
Use `A` and the formula you proposed previously to transform the coefficient matrix back to the AO basis. Confirm that the resulting matrix appears reasonable, i.e., similar size and magnitude

```
# Transform the coefficient matrix back into AO basis
# Transform the coefficient matrix back into AO basis
C = A.dot(C_p)
print(C)
```

```
print("\nThe size of C is :",C.shape)
print("Frobenius norm of C to check magnitude : ||C||_F = Tr[C^T C]
    =", np.trace((C.T).dot(C)))
```

```
[[-1.00154358e+00  2.33624458e-01 -3.02733347e-16 -8.56842079e-02
   3.63414278e-15 -4.82226017e-02  9.45116473e-16]
 [ 7.18933084e-03 -1.05793876e+00  1.40864302e-15  3.60110465e-01
  -1.53723457e-14  4.63121174e-01 -9.15741996e-15]
 [ 2.67129883e-04 -4.27284243e-01 -3.00096682e-15 -9.39942475e-01
   4.04447865e-14  2.12940092e-01 -5.11420285e-15]
 [ 0.00000000e+00 -3.33066907e-16  3.57353036e-16 -4.30211422e-14
  -1.00000000e+00 -3.33066907e-16  5.55111512e-17]
 [-2.15774773e-17  6.88978035e-17  1.06107023e+00 -3.15567076e-15
   3.95718955e-16 -6.17464044e-15 -2.96507060e-01]
 [-1.82134850e-03  1.49253289e-01  1.37720978e-01  3.78578935e-02
  -1.61997318e-15 -7.80700283e-01 -8.50140251e-01]
 [-1.82134850e-03  1.49253289e-01 -1.37720978e-01  3.78578935e-02
  -9.93671961e-16 -7.80700283e-01  8.50140251e-01]]

The size of C is : (7, 7)
Frobenius norm of C to check magnitude : ||C||_F = Tr[C^† C] = 2.933564513151939
```

Exercise 19
Build the density matrix, `D`, from the occupied orbitals, `C_occ`, using the function `np.einsum()`. **Hint** Look at (**??**)

```
# Build density matrix from occupied orbitals
D = np.array(np.einsum('pi,qi->pq',C_occ.conj(),C_occ)) # replace
    this command with np.einsum() as described above
print(F'The shape of D is {D.shape}')
```

```
The shape of D is (7, 7)
```

Exercise 20
Define J in terms of the density matrix, `D`, and the electron repulsion integral tensor, `I`, using `np.einsum()`.

```
#Define J
J = np.einsum('rs,pqrs->pq',D,I) # use np.einsum here
```

Exercise 21
Define K in terms of the density matrix, `D`, and the electron repulsion integral tensor, `I`, using `einsum()`.

```
#Define K
K = np.einsum('rq,pqrs->ps',D,I) # use np.einsum here
```

Exercise 22
Define F in terms of H, J, and K. (Recall The Hartree-Fock procedure)

```
#Define F as a function of H, J, and K
F = H + 2*J - K # insert code here
```

Exercise 23
Calculate the SCF energy based on H, F, and D using `np.einsum()`.

```
E_nuc = mol.nuclear_repulsion_energy()
SCF_E = E_nuc + np.einsum('pq,pq->',H + F,D) # insert your code
    here, don't forget to use E_nuc
print(F'Energy = {SCF_E:.8f}')
```

```
Energy = -73.28579644
```

Exercise 24
Based on the result of the calculation in **??**, is this a reasonable answer?

We foud previously :
`The Hartree-Fock ground state energy of the water is: -74.94207989868096 Eh`
The relative error is : $e = \frac{-73.285780+74.94208}{74.94208} \equiv 2.21\%$, which is significant. This means that our initial guess of the Fock matrix being the hamiltonian H leads to an SCF energy that is not a reasonable answer.

Exercise 25
Describe a procedure (i.e. identify the steps) that will update coefficients and compute a new density matrix based on the updated values of the Fock matrix.

We obtained the new Fock matrix $F = H+2J-K$. We should now take $F' = AFA$, find its eigenvalues and eigenvectors which give the coefficient matrix C' and then $C = AC'$ which are the coefficient that we want to optimize in order to minimize SCF Energy. From that we can reavaluate the important quantites such as the electron density matrix D which is now refined compared to before and recalculate SCF energy to check for convergence. Each iteration, the energy decreases by taking the last F since the new one incororates better electron interactions.

Exercise 26
Using the procedure proposed above, calculate the updated coefficients

```
# ==> Nuclear Repulsion Energy <==
E_nuc = mol.nuclear_repulsion_energy()

# ==> SCF Iterations <==
```

```
# Pre-iteration energy declarations
SCF_E = 0.0
E_old = 0.0

# ==> Set default program options <==
# We continue recalculating the energy until it converges to the level we specify.
# The varible ‘E_conv‘ is where we set this level of convergence. We also set a
# maximum number of iterations so that if our calculation does not converge, it
# eventually stops and lets us know that it did not converge.
# Maximum SCF iterations
MAXITER = 40
# Energy convergence criterion
E_conv = 1.0e-6

print('==> Starting SCF Iterations <==\n')

# Begin Iterations
for scf_iter in range(1, MAXITER + 1):

    # Build Fock matrix (meaning define J, K with density matrix and then define F with J and k)

    # <your code here>
    J = np.einsum('rs,pqrs->pq',D.conj(),I)
    K = np.einsum('rq,pqrs->ps',D.conj(),I)
    F = H + 2*J - K


    # Compute SCF energy (don't forget E_nuc!)

    SCF_E = E_nuc + np.einsum('pq,pq->',H + F,D) #<your formula here>

    print(F'SCF Iteration {scf_iter}: Energy = {SCF_E:.8f} dE = {SCF_E - E_old:.8f}')

    # Check to see if the energy is converged.  If it is break out of the loop.
    # If it is not, set the current energy E_old

    if (abs(SCF_E - E_old) < E_conv):
        break
    E_old = SCF_E

    # Compute new coefficient & density matrices (Exercise 26)

    # <your code here>
    F_p = A.dot(F.dot(A))

    # find e and C_p
    e, C_p = np.linalg.eigh(F_p)

    # find C
    C = A.dot(C_p)
```

```
55
56      # Select the occupied MOs
57      C_occ = C[:, :ndocc]
58
59      # Update the density matrix
60      D = np.einsum('pi,qi->pq', C_occ.conj(), C_occ)
61
62      # MAXITER exceeded?
63      if (scf_iter == MAXITER):
64          psi4.core.clean()
65          raise Exception("Maximum number of SCF iterations exceeded.
        ")
66
67  # Post iterations
68  print('\nSCF converged.')
69  print(F'Final RHF Energy: {SCF_E:.6f} [Eh]')
```

```
==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098

SCF converged.
Final RHF Energy: -74.942080 [Eh]
```

```
1  # ==> Compare our SCF to Psi4 <==
2  # Call psi4.energy() to compute the SCF energy
3  SCF_E_psi = psi4.energy('SCF')
4  psi4.core.clean()
5
6  print(f"PSI4 {SCF_E_psi:.6f}  Ours {SCF_E:.6f}   Absolute
       difference {np.abs(SCF_E-SCF_E_psi)}")
```

```
PSI4 -74.942080 Ours -74.942080 Absolute difference 2.9805295298501733e-07
```

Bonus Exercise 27
Modify the value of E_conv and describe its effect the number of iterations.Provide your code, the output of the SCF calculation and the number of iterations.

```
1  E_conv_values = [1e-3, 5e-4, 1e-4, 5e-5, 1e-6, 5e-7, 1e-8, 5e-9, 1e
       -10, 1e-12]
2
```

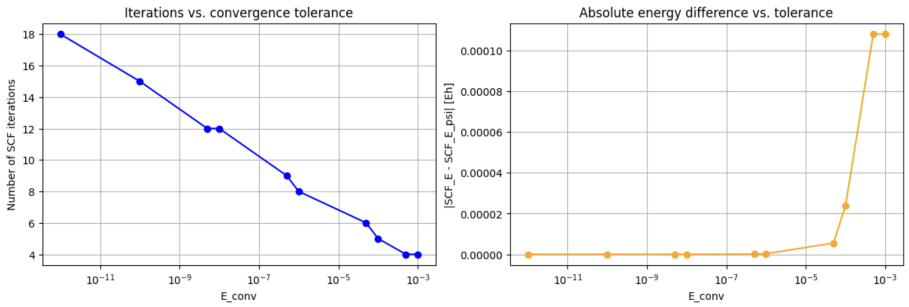
```
iterations_per_econv = []
abs_diffs_per_econv = []

for E_conv in E_conv_values:
    print(f"\n\n===== Running SCF with E_conv = {E_conv:.1e} =====\
    n")

    # We restart the whole process
    # Guess for the Fock matrix
    F = H # Replace

    # Transformed Fock matrix
    F_p =  A.dot(F.dot(A)) # Replace

    # Diagonalize F_p for eigenvalues & eigenvectors with NumPy
    e, C_p =  np.linalg.eigh(F_p) # Replace

    # Retrieve C
    C = A.dot(C_p)

    C_occ = C[:, :ndocc]

    # Build density matrix from occupied orbitals
    D = np.array(np.einsum('pi,qi->pq',C_occ.conj(),C_occ))

    # Build electron repulsion integral (ERI) Tensor
    I = np.asarray(mints.ao_eri())

    #Define J
    J = np.einsum('rs,pqrs->pq',D.conj(),I) # use np.einsum here

    #Define K
    K = np.einsum('rq,pqrs->ps',D.conj(),I) # use np.einsum here

    #Define F as a function of H, J, and K
    F = H + 2*J - K # insert code here

    E_nuc = mol.nuclear_repulsion_energy()
    SCF_E = E_nuc + np.einsum('pq,pq->',H + F,D)

    # insert remaining steps here, you should end with a new C
    # transform F to the orthonormal basis
    F_p = A.dot(F.dot(A))

    # find e and C_p
    e, C_p = np.linalg.eigh(F_p)

    # find C
    C = A.dot(C_p)

    # Select the occupied MOs
    C_occ = C[:, :ndocc]


    # Update the density matrix
    D = np.einsum('pi,qi->pq', C_occ.conj(), C_occ)

```

```
    # ==> Nuclear Repulsion Energy <==
    E_nuc = mol.nuclear_repulsion_energy()

    # ==> SCF Iterations <==
    # Pre-iteration energy declarations
    SCF_E = 0.0
    E_old = 0.0

    # ==> Set default program options <==
    # Maximum SCF iterations
    MAXITER = 40
    # Energy convergence criterion comes from the loop variable
    E_conv

    print('==> Starting SCF Iterations <==\n')

    # Begin Iterations
    for scf_iter in range(1, MAXITER + 1):

        # Build Fock matrix
        J = np.einsum('rs,pqrs->pq',D.conj(),I)
        K = np.einsum('rq,pqrs->ps',D.conj(),I)
        F = H + 2*J - K

        # Compute SCF energy (don't forget E_nuc!)
        SCF_E = E_nuc + np.einsum('pq,pq->',H + F,D)

        print(F'SCF Iteration {scf_iter}: Energy = {SCF_E:.8f} dE =
     {SCF_E - E_old:.8f}')

        # Convergence check
        if (abs(SCF_E - E_old) < E_conv):
            iter_count = scf_iter  # record how many iterations
    this run took
            break
        E_old = SCF_E

        # New coefficients & density
        F_p = A.dot(F.dot(A))
        e, C_p = np.linalg.eigh(F_p)
        C = A.dot(C_p)
        C_occ = C[:, :ndocc]
        D = np.einsum('pi,qi->pq', C_occ.conj(), C_occ)

        # MAXITER exceeded?
        if (scf_iter == MAXITER):
            psi4.core.clean()
            raise Exception("Maximum number of SCF iterations
    exceeded.")

    # Post iterations
    print('\nSCF converged.')
    print(F'Final RHF Energy: {SCF_E:.6f} [Eh]')

    # ==> Compare our SCF to Psi4 <==
    SCF_E_psi = psi4.energy('SCF')
    psi4.core.clean()
```

```
    abs_diff = np.abs(SCF_E - SCF_E_psi)
    print(f"PSI4 {SCF_E_psi:.6f}  Ours {SCF_E:.6f}   Absolute
    difference {abs_diff}")

    # Save metrics for this tolerance
    iterations_per_econv.append(iter_count)
    abs_diffs_per_econv.append(abs_diff)

# === Plots: side-by-side ===
fig, axes = plt.subplots(1, 2, figsize=(12, 4), constrained_layout=
    True)

# Left: iterations vs E_conv
axes[0].plot(E_conv_values, iterations_per_econv, marker='o', color
    ="b")
axes[0].set_xscale('log')
axes[0].set_xlabel('E_conv')
axes[0].set_ylabel('Number of SCF iterations')
axes[0].set_title('Iterations vs. convergence tolerance')
axes[0].grid(True)

# Right: |SCF_E - SCF_E_psi| vs E_conv
axes[1].plot(E_conv_values, abs_diffs_per_econv, marker='o',color =
    "orange")
axes[1].set_xscale('log')
axes[1].set_xlabel('E_conv')
axes[1].set_ylabel('|SCF_E - SCF_E_psi| [Eh]')
axes[1].set_title('Absolute energy difference vs. tolerance')
axes[1].grid(True)

plt.show()
```

Here is the track of the SCF iterations for the following values :

```
E_conv_values = [1e-3, 5e-4, 1e-4, 5e-5, 1e-6, 5e-7, 1e-8, 5e-9, 1e
    -10, 1e-12]
```



We observe that decreasing the threshold E_{conv} leads to higher accuracy (min absolute error of $3.13 \cdot 10^{-13}$) and longuer computation time (18 iterations). Therefore E_{conv} plays a substantial role in terms of accuracy and convergence time, we have to make a trade-off between the two. For such small molecules we don't have much problems but for more complicated molecules we can reasonably extend this notion of trade-off.

```
===== Running SCF with E_conv = 1.0e-03 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425

SCF converged.
Final RHF Energy: -74.941972 [Eh]
PSI4 -74.942080  Ours -74.941972   Absolute difference 0.00010793216969773312


===== Running SCF with E_conv = 5.0e-04 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425

SCF converged.
Final RHF Energy: -74.941972 [Eh]
PSI4 -74.942080  Ours -74.941972   Absolute difference 0.00010793216969773312


===== Running SCF with E_conv = 1.0e-04 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407

SCF converged.
Final RHF Energy: -74.942056 [Eh]
PSI4 -74.942080  Ours -74.942056   Absolute difference 2.3866800034966218e-05
```

```
===== Running SCF with E_conv = 5.0e-05 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836

SCF converged.
Final RHF Energy: -74.942074 [Eh]
PSI4 -74.942080  Ours -74.942074   Absolute difference 5.509059405994776e-06


===== Running SCF with E_conv = 1.0e-06 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098

SCF converged.
Final RHF Energy: -74.942080 [Eh]
PSI4 -74.942080  Ours -74.942080   Absolute difference 2.9805295298501733e-07
```

```
===== Running SCF with E_conv = 5.0e-07 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098
SCF Iteration 9: Energy = -74.94207983 dE = -0.00000023

SCF converged.
Final RHF Energy: -74.942080 [Eh]
PSI4 -74.942080  Ours -74.942080   Absolute difference 6.938856245142233e-08


===== Running SCF with E_conv = 1.0e-08 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098
SCF Iteration 9: Energy = -74.94207983 dE = -0.00000023
SCF Iteration 10: Energy = -74.94207988 dE = -0.00000005
SCF Iteration 11: Energy = -74.94207989 dE = -0.00000001
SCF Iteration 12: Energy = -74.94207990 dE = -0.00000000

SCF converged.
Final RHF Energy: -74.942080 [Eh]
PSI4 -74.942080  Ours -74.942080   Absolute difference 8.757581326790387e-10
```

```
===== Running SCF with E_conv = 5.0e-09 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098
SCF Iteration 9: Energy = -74.94207983 dE = -0.00000023
SCF Iteration 10: Energy = -74.94207988 dE = -0.00000005
SCF Iteration 11: Energy = -74.94207989 dE = -0.00000001
SCF Iteration 12: Energy = -74.94207990 dE = -0.00000000

SCF converged.
Final RHF Energy: -74.942080 [Eh]
PSI4 -74.942080  Ours -74.942080   Absolute difference 8.757581326790387e-10


===== Running SCF with E_conv = 1.0e-10 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098
SCF Iteration 9: Energy = -74.94207983 dE = -0.00000023
SCF Iteration 10: Energy = -74.94207988 dE = -0.00000005
SCF Iteration 11: Energy = -74.94207989 dE = -0.00000001
SCF Iteration 12: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 13: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 14: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 15: Energy = -74.94207990 dE = -0.00000000

SCF converged.
Final RHF Energy: -74.942080 [Eh]
PSI4 -74.942080  Ours -74.942080   Absolute difference 1.1169731806148775e-11
```

Figure 2: SCF iterations for different values of E_{conv}

```
===== Running SCF with E_conv = 1.0e-12 =====

==> Starting SCF Iterations <==

SCF Iteration 1: Energy = -74.82812526 dE = -74.82812526
SCF Iteration 2: Energy = -74.93548796 dE = -0.10736270
SCF Iteration 3: Energy = -74.94147771 dE = -0.00598975
SCF Iteration 4: Energy = -74.94197197 dE = -0.00049425
SCF Iteration 5: Energy = -74.94205603 dE = -0.00008407
SCF Iteration 6: Energy = -74.94207439 dE = -0.00001836
SCF Iteration 7: Energy = -74.94207862 dE = -0.00000423
SCF Iteration 8: Energy = -74.94207960 dE = -0.00000098
SCF Iteration 9: Energy = -74.94207983 dE = -0.00000023
SCF Iteration 10: Energy = -74.94207988 dE = -0.00000005
SCF Iteration 11: Energy = -74.94207989 dE = -0.00000001
SCF Iteration 12: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 13: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 14: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 15: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 16: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 17: Energy = -74.94207990 dE = -0.00000000
SCF Iteration 18: Energy = -74.94207990 dE = -0.00000000

SCF converged.
Final RHF Energy: -74.942080 [Eh]
PSI4 -74.942080  Ours -74.942080   Absolute difference 3.126388037344441e-13
```