Calculation of molecular electric dipole moments of light and moderately heavy molecules using relativistic VQE algorithm

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The quantum-classical hybrid Variational Quantum Eigensolver (VQE) algorithm is recognized to be the most suitable approach to obtain ground state energies of quantum many-body systems in the Noisy Intermediate Scale Quantum era. In this work, we extend the VQE algorithm to the relativistic regime and carry out quantum simulations to obtain ground state energies as well as molecular permanent electric dipole moments of single-valence diatomic molecules, which include light and moderately heavy systems.

Keywords: VQE algorithm, relativistic effects, molecular electric dipole moments

I. INTRODUCTION

Following Feynman’s proposal [1] in 1982, the field of quantum computing has advanced significantly, and a lot of work has gone into developing quantum algorithms [2, 3], which have applications in search and optimization [4, 5], solutions to systems of linear equations [6], quantum machine learning [7, 8], and simulation of quantum systems [9–12]. However, there is tremendous potential for achieving quantum advantage in the simulation of quantum many-body systems, such as atoms and molecules, on quantum computers [13–14]. Even with the current finest supercomputers in the market, this problem is highly challenging to simulate, since the computational cost needed to describe such states grows exponentially with the size of the system. Quantum devices can make full use of inherent quantum properties, such as the fact that the wavefunction of an atom or molecule is entangled, to gain an exponential speed-up over the classical computers [15, 16].

The quantum phase estimation algorithm [16] was proposed to efficiently solve atomic and molecular problems on a quantum computer. However, since even for medium-sized systems, this algorithm requires many gates hence leading to deep circuits, this approach is strongly constrained by noise and decoherence effects that are prevalent in the current noisy intermediate scale quantum (NISQ) era. However, the classical-quantum hybrid variational quantum eigensolver (VQE) algorithm addresses this issue with relatively shallow circuits, thus allowing it to be run on the available NISQ [17] devices.

Thus far, the VQE algorithm has predominantly been employed to calculate ground state energies and first ionization energies of atomic, molecular and ionic systems [18–24]. It has also been experimentally realized on different quantum hardware platforms [25–36]. However, there are not many works that calculate atomic and molecular properties besides energies. Further, to the best of our knowledge, only one work treats relativistic effects in such systems [37].

In this work, we calculate the permanent electric dipole moments (PDMs) of single valence molecular systems along with their ground state energies, by implementing the VQE algorithm in a relativistic framework. Besides one light molecule (BeH), we choose a moderately heavy one (SrH), where relativistic effects become noticeable.

We discuss the theory and the adopted methodology in this work in Section II. This is followed by Section III, where we show the results obtained for the ground state energies and PDMs of the chosen molecules using...
the relativistic VQE algorithm. We finally conclude in Section IV.

We expect that our work would be a first step in determining the PDMs of more complex molecules, such as SrF and BaF [38], which are laser coolable and can be trapped in optical lattices [39]. The PDM itself is a useful property and helps one to determine, for example, the dipole-dipole interaction in the low-temperature regime, which can give rise to novel quantum states of matter like the supersolid state, thereby enabling one to understand some fundamental aspects of condensed matter physics.

II. THEORY AND METHODOLOGY

According to the Rayleigh-Ritz variational principle [40], by varying certain parameters, one can optimize the problem at hand (an appropriately chosen cost function) and the obtained energy is an upper bound to the true ground state energy. Therefore, for a given many-body Hamiltonian $\hat{H}$, and a trial wave function $|\Psi(\theta)\rangle$ with variational parameters $\{\theta\} \subseteq \{\theta_1, \theta_2, \ldots\}$, the ground state energy $E_0$ of the quantum many-body system is bounded by

$$E(\theta) = \frac{\langle \Psi(\theta) | \hat{H} | \Psi(\theta) \rangle}{\langle \Psi(\theta) | \Psi(\theta) \rangle} \geq E_0.$$  

The trial wave function $|\Psi(\theta)\rangle$, also called the ansatz wave function should be realizable as a quantum circuit so that it can be executed on a quantum device. Since only unitary operations can be performed on a quantum computer, we choose our ansatz to be the unitary coupled cluster (UCC) ansatz [41,42]. The general form of the many-body wave function is written as

$$|\Psi(\theta)\rangle = \hat{U}(\theta)|\Phi_0\rangle = e^{T - T^\dagger}|\Phi_0\rangle = e^{\hat{T} - \hat{T}^\dagger}|\Phi_0\rangle,$$

where, $|\Phi_0\rangle$ is the initial/reference Hartree-Fock state, $\hat{U}(\theta)$ is the UCC operator and where, $\hat{T}$ and $\hat{T}^\dagger$ are the fermionic excitation and de-excitation operators respectively. In our work, we have only considered single (S) and double (D) excitations. In the UCC approach, the usual CC method is modified to be both variational and unitary, and it can therefore be implemented on a quantum computer.

The molecular many-body Hamiltonian $\hat{H}$ can be written in the second quantized notation as

$$\hat{H} = \sum_{p,q} t_{pq} \hat{a}_p^\dagger \hat{a}_q + \frac{1}{2} \sum_{p,q,r,s} v_{pqrs} \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_r \hat{a}_s, \quad (4)$$

where $\hat{a}_p^\dagger$ and $\hat{a}_p$ are creation and annihilation operators, which create and annihilate an electron in spin orbitals $p$ and $q$ respectively. The summation is over the number of spin orbitals, which depends on the choice of single particle basis set used. For the non-relativistic case, the one- and two-electron integrals $t_{pq}$ and $v_{pqrs}$, are evaluated on a traditional computer using the Pyscf [45] package.

To express the Hamiltonian given by eqn (4) on a quantum computer, it is necessary to convert the strings of creation and annihilation operators to unitary operators. The Pauli operators are the most convenient ones for facilitating this transformation. We use Jordan–Wigner mapping to transform the second quantized operators in eqn (3) to tensor products of Pauli operators. The Hamiltonian in eqn (4) now takes the form

$$\hat{H'} = \sum_j M \alpha_j \hat{P}_j,$$

where $\alpha_j$ are real scalar coefficients which depend on $t_{pq}$ and $v_{pqrs}$. $\hat{P}_j$ are Pauli strings represented by tensor products of Pauli operators $\{I, X, Y, Z\}$ and $M$ denotes the number of Pauli strings in the Hamiltonian. Now, eqn (3) can be written as

$$E(\theta) = \sum_j M \alpha_j \langle \Phi'_0 | U^\dagger(\theta) \hat{P}_j U(\theta) | \Phi'_0 \rangle. \quad (6)$$

Each term in eqn (6) corresponds to the expectation value of a Pauli string $\hat{P}_j$, which will be evaluated on a quantum computer, while the summation and energy minimization will be done on a classical computer. The energy is minimized by updating the parameters in an iterative process using an appropriate optimization algorithm. In this work, we start with zero initial parameters and employ the SLSQP classical optimizer [47] to obtain the optimal VQE parameters.

For the relativistic calculations, we begin with the Dirac-Coulomb Hamiltonian, which is given by

$$\hat{H}_{DC} = \sum_i (c \overrightarrow{p}_i^2 + \beta m_i c^2) + \sum_i V_{\text{nuc}}(r_i) + \sum_{i \neq j} \frac{1}{2} \frac{e^2}{r_{ij}},$$

where $c$ is the speed of light, $m_i$ is the mass of particle $i$, $\beta$ is the fine structure constant, and $r_{ij}$ is the distance between particles $i$ and $j$.
where \( \hat{\sigma} = \begin{pmatrix} 0 & \hat{\sigma} \\ \hat{\sigma} & 0 \end{pmatrix} \), \( \beta = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \). \( \hat{\sigma} \) are the Pauli matrices and \( I \) is the \( 2 \times 2 \) identity matrix. When the Dirac-Coulomb Hamiltonian is converted to its second quantized form, \( t_{pq} \) in eqn (4) is obtained by taking the one-particle matrix elements of the Dirac Hamiltonian supplemented by the potential energy of the electron due to the nucleus.

We use the relativistic integrals generated by DIRAC22 [46], in place of Pyscf’s [15] non-relativistic integrals to construct the Dirac-Coulomb Hamiltonian. Thereafter, we use this Hamiltonian to obtain the relativistic UCCSD-VQE energy by employing the state-vector backend.

The PDM of a diatomic molecule can be obtained by

\[
\langle \hat{D} \rangle = \langle \Psi(\theta_\ast)|\hat{D}|\Psi(\theta_\ast)\rangle; \text{ where } |\Psi(\theta_\ast)\rangle \text{ is the ground state wavefunction which is constructed from the converged \( \theta_\ast \) amplitudes (denoted by the subscript, ‘\( \ast \)’) of the VQE algorithm.}
\]

The dipole moment operator \( \hat{D} \) contains two terms; the nuclear and the electronic terms. In this work, the nuclear part contains only one term, since we have chosen one of the two atoms in the diatomic molecule to be positioned at the origin. Therefore, the dipole moment operator \( \hat{D} \) within the Born-Oppenheimer approximation is expressed as

\[
\hat{D} = e \left( Z_N R_N - \sum_j r_j \right), \tag{8}
\]

where \( e \) is the electronic charge, \( r_j \) is the position coordinate of the \( j^{th} \) electron from the origin, \( R_N \) is the bond length of the molecule, and \( Z_N \) is the nuclear charge of the second atom which is not at the origin. We obtained both the non-relativistic and relativistic dipole integrals from the DIRAC22 code and calculated the dipole moment of the diatomic molecules by taking the expectation value of the dipole operator with the ground state wavefunction.

### III. RESULTS AND DISCUSSION

This section presents and discusses our results for the PDMs and ground state energies of the Beryllium Hydride (BeH) and Strontium Hydride (SrH) molecules in the contracted 3-21G basis sets. A basis set can be viewed as a set of atomic orbitals. In the minimal STO-3G basis, each atomic orbital is built out of a linear combination of three Gaussians (with the linear combination defined as a basis function) in order to mimic a Slater-type orbital. In comparison to the STO-3G basis, more correlation effects can be captured if more than one basis function is used for each valence orbital. In the 3-21G basis set, the core orbitals are each built out of one basis function (a linear combination of three Gaussians), whereas in the two valence orbitals, the first is composed of two basis functions and the second is composed of just one. Both BeH and SrH are single valence molecules. To that end, we have made appropriate non-trivial changes in Qiskit [48] to adapt the code to handle such systems.

We now proceed to investigate the interplay of relativistic and correlation effects through our theoretical studies of the ground state energies and PDMs of BeH and SrH molecules. In order to do so, we perform seven calculations per molecule using mean field (HF and DF), quantum-classical hybrid UCCSD-VQE algorithm (Existing non-relativistic (NR) codes, our NR and relativistic (rel) codes), and FCI (best possible result within a single part basis) in the NR and rel regimes. We first focus on the contributions from the relativistic effects, followed by those from correlation effects. We can determine the relativistic effects of the desired molecule by comparing the HF and DF values, or UCCSD-VQE NR and rel results from our codes, or FCI NR and rel results. We also give percentage fraction differences between the HF and FCI, as well as the HF and UCCSD-VQE methods, to get an estimate of the correlation effects that have been captured by the VQE method. After determining the relativistic and correlation effects, we examine the ‘net’ effect due to their interplay, resulting from cancellations. To test the proper implementation of our code, we compare the UCCSD-VQE results between the Qiskit NR and our NR methods. We present all the results with more than one basis function are used for each valence orbital.

| Method                          | Energy       | PDM  |
|--------------------------------|--------------|------|
| HF                             | -15.058938   | 0.30 |
| DF                             | -15.061415   | 0.30 |
| UCCSD-VQE (Existing NR codes)  | -15.074583   | 0.19 |
| UCCSD-VQE (Our NR codes)       | -15.074583   | 0.19 |
| UCCSD-VQE (Our Rel codes)      | -15.076860   | 0.19 |
| FCI (NR)                       | -15.074781   | 0.19 |
| FCI (Rel)                      | -15.077058   | 0.19 |
| Best available classical data  | 0.24         |      |

Table I. Table 1 shows ground state energies and PDMs of the BeH molecule from different methods in the 3-21G basis set. The list of abbreviations used are HF: Hartree-Fock, DF: Dirac-Fock, UCCSD-VQE: VQE with UCCSD ansatz, NR: non-relativistic, Rel: relativistic, FCI: Full Configuration Interaction. Note that ‘Existing NR codes’ refers to results obtained from Qiskit with the UCCSD-VQE calculations. We obtained FCI results by using the numpy eigensolver. The energy is in units of Hartree, whereas the PDM is given in Debye.
Table II. Table 2 shows ground state energies and PDMs of 
SrH molecule using different methods in the 3-21G basis set. 
The notations are the same as those in Table 1.

| Method                          | Energy   | PDM  |
|---------------------------------|----------|------|
| HF                              | -3117.615326 | 2.58 |
| DF                              | -3161.398690 | 2.49 |
| UCCSD-VQE (Existing NR codes)   | -3117.632870 | 2.08 |
| UCCSD-VQE (Our NR codes)       | -3117.632870 | 2.08 |
| UCCSD-VQE (Our Rel codes)      | -3161.403952 | 2.00 |
| FCI (NR)                        | -3117.633009 | 2.07 |
| FCI (Rel)                       | -3161.404042 | 2.00 |

are given in Table I. The equilibrium bond length of 
the BeH molecule is taken to be 1.342 Å [49]. 
In order to perform the computation with 16 qubits, 
six of the eighteen virtual spin orbitals have not been 
considered. Since BeH is a light molecule, the relativistic 
effects are not expected to be large, as is the case here. The difference between the NR and the rel 
results, if correlation effects are not taken into consideration, are 2.5 mHa at the mean-field level, and 2.3 mHa for UCCSD-VQE, and FCI approaches, which 
correspond to percentage fraction differences of 0.02 percent for all the three cases. The correlation effects captured 
by the NR Hamiltonian (difference between HF 
and UCCSD-VQE energies) amounts to 15.6 mHa, and the difference between HF and FCI results is 15.8 mHa. 
In the relativistic case, the correlation effects are found 
to be 15.4 mHa (difference between rel UCCSD-VQE 
and DF), and 15.6 mHa (difference between rel FCI 
and DF results). Therefore, the combined relativistic 
correlation effects is about 18 mHa.

We now report the observed trends in the PDM. There is no difference between the HF and the DF PDM 
values for the BeH molecule. The relativistic effects are 
therefore negligible here within the specified basis. The effect of electron correlation is to reduce the PDM, with 
the percentage fraction difference being 36.67 percent 
with respect to VQE, and FCI methods.

Table II shows the ground state energies and PDMs for the SrH molecule determined by seven different 
methods in the 3-21G basis. The bond length of the 
SrH molecule is taken to be 2.1461 Å [49]. In 
our calculation, forty spin orbitals (including core and 
virtual orbitals) have not been considered in order to 
make the SrH molecule a 16 qubit calculation. Since 
SrH is moderately heavy compared to BeH, we can 
expect larger relativistic effects in the former molecule. At 
the mean-field level of theory, UCCSD-VQE, and FCI 
levels, the relativistic effects account for 43.78 Ha, 43.77 Ha, and 43.77 Ha, which correspond to percentage fraction 
differences of 1.40 percent in all three cases. The correlation effects that we capture are 17.54 mHa (dif-
ference between UCCSD-VQE and HF) and 17.68 mHa (difference between FCI and HF methods). For the relativistic case, the correlation effects are 5.26 mHa (difference between rel UCCSD-VQE and DF) and 5.35 mHa (difference between rel FCI and DF). The relativistic 
and correlation effects add up to 43.79 Ha. This illustrates the complex nature of the calculations in quantum 
many-body theory, by virtue of the interplay between relativistic and correlation effects. 

Relativistic effects were discernible clearly from the computations of the PDM of SrH since it is a relatively 
heavy molecule. At the mean-field, UCCSD-VQE, and 
FCI levels respectively, we obtained relativistic effects with percentage fractions of 3.49, 3.85, and 3.38. For 
the NR case, the correlation effects lower the value of 
PDM with percentage fractions of 19.38 and 19.77 
for the UCCSD-VQE and FCI methods, while for the rel case the corresponding values in the reduction of the 
PDM are 19.68 for both the many-body methods. 
Therefore, the relativistic and correlation effects add up to give a total of 22.49 percentage fraction difference.

IV. CONCLUSION

The ground state energies and molecular electric 
dipole moments of a light and a moderately heavy 
molecular system have been calculated using both the 
relativistic and non-relativistic versions of the VQE 
algorithms. We find from our simulations that the relativistic VQE algorithm is capable of capturing relativistic 
effects in ground state energies to within a precision 
of 2 mHa for BeH (99.99 percentage agreement between 
our relativistic VQE calculations and relativistic FCI), 
and 0.09 mHa (99.99 percentage agreement between 
our relativistic VQE calculations and relativistic FCI) 
for SrH, and in PDMs with a precision of 100 percent 
(within two decimal places in units of Debye) for both 
BeH and SrH. We anticipate that with advancements 
in quantum hardware, relativistic VQE algorithm will 
be able to handle heavier molecular systems and open 
new avenues for novel applications such as probing new 
physics beyond the Standard Model of elementary 
particles.

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