Abstract

Quasi-classical treatment of atomic structure is the study of atoms using a classical Hamiltonian modified to incorporate quantum effects using momentum-dependent pseudopotentials. These potentials simulate the effect of Heisenberg Uncertainty Principle and the Pauli Exclusion Principle by excluding the regions of phase space forbidden by these principles. This treatment is attractive owing to the reduced computational costs involved as compared to a complete quantum mechanical treatment of many electron atoms. The ground state energies of the first three noble gas elements Helium, Neon, and Argon have been determined using this treatment following [1,3] and show close agreement with the corresponding Hartree-Fock ground state energies. Significance of the parameters used in the model to obtain accurate energy values has been studied and their inter-dependence is reported for the ground states of Argon and Neon. This result suggested a possible functional relation between the parameters and the corresponding quantum numbers characterizing the state which has been confirmed in case of Hydrogen atom.

Minimization

Broyden-Fletcher-Goldfarb-Shanno (BFGS) Quasi-Newton method [4] was adopted for minimizing $H_{QC}$ to determine ground state configuration -
1. Search direction:
   \[ p_k = -B_k^{-1} \nabla f(x_k) \]
2. Step length:
   \[ \alpha_k \in R^+ \rightarrow \min \phi(\alpha_k) \]
   \[ \phi(\alpha_k) = f(x_k + \alpha_k p_k) \]
3. Variable update:
   \[ x_{k+1} = x_k + \alpha_k p_k \]
4. Hessian update:
   \[ B_{k+1} = B_k + \left( \frac{\partial^2 f}{\partial x^2} | x_{k+1} \right) - \left( \frac{\partial^2 f}{\partial x^2} | x_k \right) \]

Results

I. Ground State Energies

<table>
<thead>
<tr>
<th>Element</th>
<th>$\Omega_H$</th>
<th>$\Omega_P$</th>
<th>$E_H$</th>
<th>$E_P$</th>
<th>$\Delta E$</th>
<th>$\Delta E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>4</td>
<td>0.95</td>
<td>-0.5</td>
<td>-0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
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<td>1.13</td>
<td>-2.8567</td>
<td>-2.8617</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ne</td>
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<td>1.19</td>
<td>-1.28594</td>
<td>-1.28617</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ar</td>
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<td>-526.4698</td>
<td>-526.8175</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Good agreement between quantum mechanical and quasi-classical results

II. Inter-dependence of $\epsilon_H$ and $\epsilon_P$

Conclusions & Future Work

- Inter-dependence of the parameters for ground states of Argon and Neon is found to be of elliptic form indicating a similar behavior for heavier noble gas elements
- Excited state energies of Hydrogen atom were determined suggesting a similar possibility for other elements
- Studying the parameter inter-dependence and determining the excited state energies of more complex atoms will be the subject of future work.

References