Quasi-Classical Study of Atomic States

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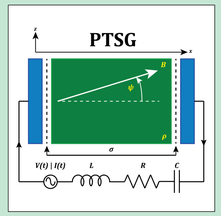


Abstract

Quasi-classical treatment of atomic structure is the study of atoms using a classical Hamiltonian modified to incorporate quantum effects using momentum dependent pseudo-potentials. 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.

Formulation

Quasi-classical Hamiltonian of an N electron atom [1,2]:

$$\boldsymbol{H_{QC} = H_0 + V_H + V_P}$$

Classical Hamiltonian $\rightarrow$ $$H_0 = \sum_{i=1}^{N} \frac{{p_i}^2}{2} - \frac{Z}{r_i} + \frac{1}{2} \sum_{i,j\ i\neq j} \frac{1}{r_{ij}}$$

Heisenberg pseudo-potential $\rightarrow$ $$V_H = \sum_{i=1}^{N} \frac{{\varepsilon_H}^2}{4\alpha_H {r_i}^2} exp\left[\alpha_H \left(1 - \left(\frac{r_i p_i}{\varepsilon_H}\right)^4\right)\right]$$

Pauli pseudo-potential $\rightarrow$ $$V_P = \frac{1}{2} \sum_{i,j\ i\neq j} \delta_{s_i,s_j} \frac{{\varepsilon_p}^2}{4\alpha_P {r_{ij}}^2} \exp\left[\alpha_P \left(1 - \left(\frac{r_{ij} p_{ij}}{\varepsilon_p}\right)^4\right)\right]$$

$\alpha_H , \alpha_P \rightarrow$ Hardness parameters

$\varepsilon_H , \varepsilon_P \rightarrow$ Phase-space parameters

$\delta_{s_i,s_j} = 1,\ s_i = s_j$; $0,\ s_i \neq s_j$

$s_i , s_j \rightarrow$ spin numbers

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:*
   - $B_{k+1} = B_k + \left(\frac{g_k g_k'}{g_k' d_k}\right) - \left(\frac{B_k d_k d_k' B_k}{d_k' B_k d_k}\right)$

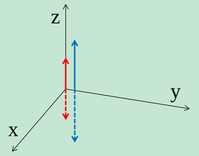
$\{x_{k+1} - x_k = d_k ,\ \nabla f(x_{k+1}) - \nabla f(x_k) = g_k\}$

Initial Guess

$[r_{0n} , p_{on}] \cong [{n^2}/{Z} ,\ {Z}/{n}]$

$\Theta_{0n} = 0, \pi$

$\phi_{0n} = 0, \pi$



Results

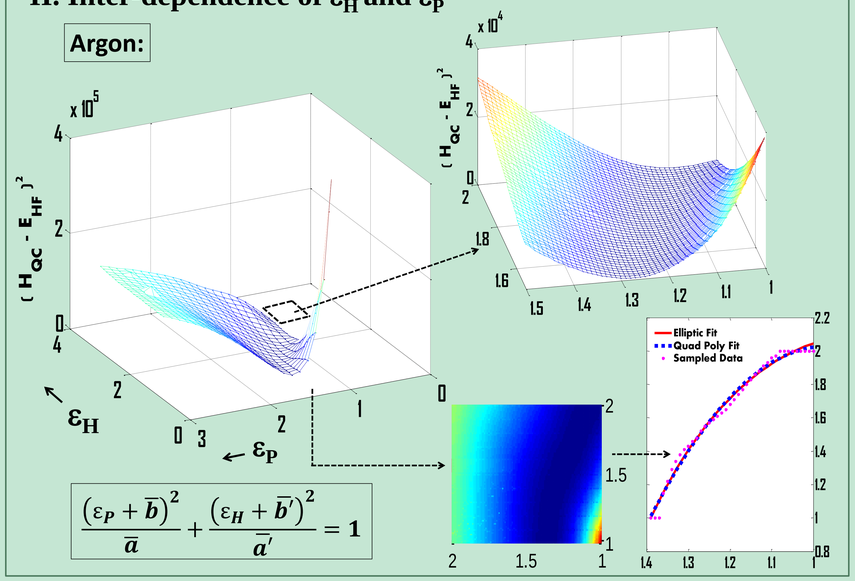
I. Ground State Energies

Element	α_H	α_P	ε_H	ε_P	H_{qc} (a.u.)	E_{HF} (a.u.)
H	4		0.95		-0.5	-0.5
He	4		0.93		-2.8567	-2.8617
Ne	2	1	1.13	1.7	-128.5943	-128.5
Ar	2	1	1.19	1.71	-526.4698	-526.8175

- Good agreement between quantum mechanical and quasi-classical results

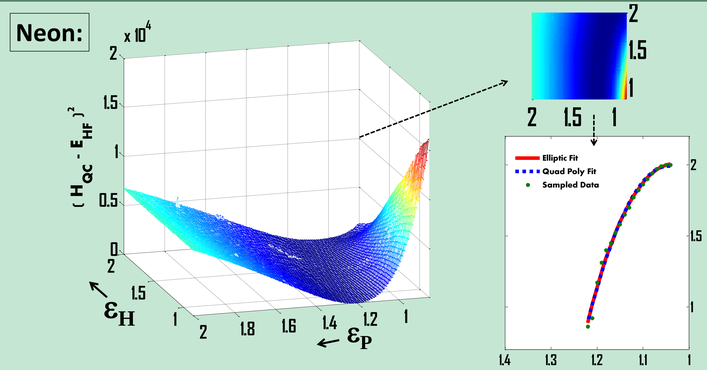
II. Inter-dependence of ε_H and ε_P

Argon:



$$\frac{(\varepsilon_P + \bar{b})^2}{\bar{a}} + \frac{(\varepsilon_H + \bar{b}')^2}{\bar{a}'} = 1$$

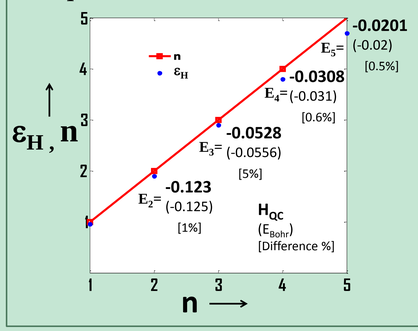
Neon:



- Physical reason for inter-dependence: possible relation to quantum numbers

III. Excited States of Hydrogen

- Determined functional relationship between ε_H and principal quantum number n to be of linear
- Obtained excited state energies in agreement with quantum mechanical results



$r.p > \varepsilon_H$

$r.p = n \rightarrow$ **Bohr Model**

$\rightarrow n > \varepsilon_H$

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

[1] J. S. Cohen, Phys. Rev. A **51**, 266 (1995)
[2] C. L. Kirschbaum and L. Wilets, Phys. Rev. A **21**, 834 (1980)
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[4] R. Fletcher, *Practical Methods of Optimization*, John Wiley & Sons (1987)