INDIAN INSTITUTE OF TECHNOLOGY GUWAHATI
PhD-17 SHORT ABSTRACT OF THESIS

Name of the Student	:	DEEPAK KUMAR
Roll Number	:	206122103
Programme of Study	:	Ph.D.

Thesis Title:
Use of Parametric Equations of Motion to Study Metastable States

Name of Thesis Supervisor(s)	:	Prof. ASHISH KUMAR GUPTA
Thesis Submitted to the Academic Division	:	CHEMISTRY
Date of completion of Thesis Viva-Voce Exam	:	25/02/2026
Key words for description of Thesis Work	:	Metastable states, Electronic Resonances, Parametric Equations of Motion, Nuclear Charge Stabilization Method, Lowest Unoccupied Molecular Orbital, Variational Collapse

---

SHORT ABSTRACT

In this thesis, a “resonance" describes an electronically metastable state, that is, a state of a metastable anion that lies energetically above the ground state of the associated neutral molecule. These metastable states can decay by losing an electron, a process known as autodetachment, or by fragmenting into a stable anion and a radical, which is called dissociative electron attachment (DEA). In studying these metastable states, it is crucial to identify the Lowest Unoccupied Molecular Orbital (LUMO), as this is the orbital that will be filled by an electron. In this context, we have developed a methodology that utilizes the Parametric Equations of Motion (PEM) with the nuclear charge stabilization method to identify the LUMO obtained from the Self-Consistent-Field (SCF) solution. This approach demonstrates stability across different basis sets, including those with diffuse functions.

However, a common issue with the SCF solution of metastable anion is that it tends to converge to a minimum energy state with an additional electron occupying the most diffuse orbital present in the basis set. As diffuse functions are increased, this solution typically converges into that of a neutral molecule and a free electron, a situation referred to as variational collapse. To address this, we have introduced a modified PEM approach in conjunction with the nuclear charge stabilization to obtain a meaningful SCF solution for a metastable anion. Here, the SCF solution for an anion with a higher nuclear charge serves as the starting point, where the anion remains

bound. The modified PEM is then executed until the additional nuclear charge approaches zero, ultimately producing the SCF solution for the metastable anion. A critical aspect of obtaining meaningful SCF solutions for metastable anions is maintaining a fixed occupation number for the orbital corresponding to the singly occupied molecular orbital throughout the PEM calculation. Furthermore, an alternative solution is provided to prevent variational collapse for metastable anions which involves removing the non-physical pseudo-continuum states at the SCF stage and implementing the process in a non-Hermitian domain, where lifetime of the electron-attached state is also accessed.

Additionally, an alternative approach named PEM-CAP has been developed for applying the Complex Absorbing Potential (CAP) at the Hartree-Fock level. This methodology was successfully applied to the uracil molecule, where identification of multiple resonances is also achieved for the first time using the nuclear charge stabilization method in conjunction with PEM. Finally, an application of parameteric equations of motion to calculate the resonances in the physical limit of $\eta = 0$ for the complex absorbing potential is also discussed. In this physical limit of $\eta = 0$, the effects of the CAP are eliminated, and complex values are still obtained for $\eta = 0$, indicating reflection-free results. To eliminate the artificial reflections caused by CAP, a methodology is introduced that employs a backward PEM-CAP approach (i.e., starting from higher CAP strength parameter η to $\eta = 0$).