



TUNA

Theoretical Unification of Nuclear Arrangements

Version 0.4.0

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Introduction

Welcome to TUNA!

Beginning as a project in my spare time, developing TUNA was intended to deepen my understanding of the theory and algorithmic implementation of quantum chemistry. It's a simple, command line-based Python program designed to calculate properties of diatomic molecules. While modest in scope, TUNA aims to be a helpful tool at the intersection of molecular physics and quantum chemistry, providing an accessible way to explore quantum mechanical calculations in small molecules.

One of TUNA's strengths is its user-friendly interface, which makes it a suitable teaching aid. With clear command line outputs, the program offers an straightforward experience for those looking to learn about quantum chemistry. On the more technical side, TUNA most unique feature is combining the calculation of potential energy surfaces with the numerical solution of the nuclear Schrödinger equation, enabling users to compare anharmonic vibrational frequencies of diatomics using a variety of (post-)Hartree--Fock methods. The program is also surprisingly efficient, considering it's written in Python.

While TUNA is modest in scope, its capability will improve in the near future. The primary long term aim is to enable it to act as a testing ground for the performance of density-functional approximations on diatomics.

One day, somebody might find the program useful and TUNA could make waves!

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Contents

1	Using TUNA	3
1.1	Input Line	3
2	Features in TUNA	4
2.1	Calculation Types	4
2.2	Methods	4
2.3	Post-SCF	5
2.4	Dispersion Correction	5
2.5	SCF Convergence Options	5
2.6	Basis Sets	6
2.7	Miscellaneous	6
3	Details of Features in TUNA	8
3.1	SCF Convergence	8
3.1.1	Level Shift	8
4	List of Parameters	9

Chapter 1

Using TUNA

1.1 Input Line

The input line reads "TUNA calculation-type: atom1 [atom2 bond-length] ! method basis-set ! parameters"

For instance an optimisation calculation with the D2 dispersion scheme on a H—He⁺ molecule starting at a bond length of 0.8 Å , using the 6-31G basis and spin-component-scaled MP2, is:

TUNA OPT: H He 0.8 ! SCS-MP2 6-31G ! D2

Chapter 2

Features in TUNA

2.1 Calculation Types

- Single point energy (SPE)
- Geometry optimisation (OPT)
- Harmonic frequency (FREQ)
- Optimisation and harmonic frequency (OPTFREQ)
- Coordinate scan (SCAN)

2.2 Methods

- Restricted Hartree–Fock
- MP2
- Spin-component-scaled MP2

2.3 Post-SCF

- Nuclear and electronic dipole moment
- Mulliken and Löwdin charges
- Mulliken and Löwdin bond orders
- Koopman's theorem electron affinity and ionisation energy
- HOMO–LUMO gap
- Electron density calculation and 3D plot
- Molecular orbitals, energies
- Rotational constant
- Centre of mass
- Thermochemistry for frequency calculations
- MP2 unrelaxed density
- MP2 natural orbital occupancies

2.4 Dispersion Correction

- D2

2.5 SCF Convergence Options

- DIIS

- Dynamic and static damping
- Slow convergence option
- Very slow convergence option
- Level shift

2.6 Basis Sets

- STO-3G
- STO-6G
- 3-21G
- 6-31G
- 6-311G
- 6-311++G

2.7 Miscellaneous

- Plot for coordinate scan
- Ghost atoms
- Temperature and pressure keywords for thermochemistry
- SCF convergence keywords
- Optimisation convergence keywords

- Identification of point group
- Approximate or exact Hessian for optimisations
- Maximum iterations keywords
- More accurate energies than ORCA

Chapter 3

Details of Features in TUNA

3.1 SCF Convergence

3.1.1 Level Shift

In level shifting, the energies of the virtual orbitals are shifted so that after diagonalisation of the Fock matrix, the occupied and virtual orbitals mix less strongly and the calculation smoothly converges.

Level shifting is applied via a parameter, b , which updates the Fock matrix by

$$\mathbf{F}' = \mathbf{F} - b\mathbf{P} \tag{3.1}$$

In TUNA, $b = 0.2$ by default. Level shift can be activated by the `LEVELSHIFT` keyword.

Chapter 4

List of Parameters

Parameter	Meaning
P	Additional print
CHARGE [int] or CH [int]	Charge
D2	D2 dispersion correction
DENSPLOT	Electron density plot
NODIIS	Turn off DIIS in SCF convergence
NODAMP	Turn off damping in SCF convergence
LEVELSHIFT	Turn on level shift in SCF convergence
SLOWCONV	Permanent high static damping
VERYSLOWCONV	Permanent very high static damping
LOOSE or LOOSESFC	Loose SCF convergence criteria
MEDIUM or MEDIUMCF	Medium SCF convergence criteria
TIGHT or TIGHTSCF	Tight SCF convergence criteria
EXTREME or EXTREMESFC	Extreme SCF convergence criteria
MAXITER [int]	Maximum SCF cycle iterations
CALCHESS	Calculate exact Hessian for optimisation
LOOSEOPT	Loose optimisation convergence criteria
MEDIUMOPT	Medium optimisation convergence criteria
TIGHTOPT	Tight optimisation convergence criteria
EXTREMEOPT	Extreme optimisation convergence criteria
GEOMMAXITER [int] or MAXGEOMITER [int]	Maximum optimisation iterations
SCANPLOT	Plot of coordinate scan potential energy surface
SCANSTEP [float]	Step size for coordinate scan
SCANNUMBER [int]	Number of steps for coordinate scan
MOREAD	Read density from previous scan step
TEMP [float]	Temperature for thermochemistry
PRES [float]	Pressure for thermochemistry