

# Recommended Settings for Jaguar

This document provides recommendations for computational settings when using Jaguar to calculate chemical properties. Basic familiarity with molecular modeling using quantum chemical software is assumed.

## Basis set

See the Molecule tab in any of the Jaguar task panels.

- Ground state geometries: use 6-31G\*\* (the default) or LACVP\*\* (when metals are present). Note that LACVP actually uses 6-31G for the elements H-Ar, but with 5 spherical harmonic d orbitals rather than the 6 Cartesian functions.
- Accurate single point energies: use cc-pVTZ(-f) or 6-311G-3df-3pd.
- Anions, excited states, intermolecular binding energies, polarizabilities, transition state geometries, or any other situation in which the electron density is likely to extend unusually far from the nuclei: include diffuse functions in whatever basis set you choose.
- Atomic ESP charges: 3-21G may be used to save time when modeling large systems.
- Studying convergence with respect to basis set size: use the series cc-pVDZ, cc-pVTZ, cc-pVQZ(-g) (you may include diffuse functions with each of these basis sets if desired).

In most situations, the small basis sets STO-3G, 3-21G, and 4-31G should be avoided.

## Theoretical method

See the Theory tab in any of the Jaguar task panels.

- Optimization of ground state geometries, thermochemical energies, zero-point energies: use B3LYP (the default).
- Transition state geometries, conformational energies, intermolecular binding energies: use M06-2X or B97-D3 (use M06 if transition metals are present).
- Tautomer energies: use M06-2X.
- Electronic excitation energies: use M06-HF.
- Atomic ESP charges: use Hartree-Fock.

In most situations, LDA functionals (such as Xalpha or SVWN) should be avoided.

DFT methods like PBE and B97-D3 are actually faster than Hartree-Fock for energies and gradients, so if saving time is essential, use one of these functionals. But for second derivative properties like vibrational frequencies, HF is faster than these DFT methods.

## Solvation energies

See the Solvation tab in any of the Jaguar task panels.

Use PBF or SM8 for energies. You must use PBF for solution-phase geometry optimizations because analytic gradients for SM8 are not available.

## Intermolecular binding energies

The binding energy for formation of the bimolecular complex A-B from molecule A and molecule B is defined as:

$$E_{\text{binding}} = E(\text{A-B}) - E(\text{A}) - E(\text{B})$$

where E is the total electronic energy. If the binding energy is required in solution, then E is the total electronic energy in solution (solution phase energy).

To obtain a binding energy which has been corrected for basis set superposition error (BSSE), use Applications > Jaguar > Counterpoise. Equivalently, you can use the script `counterpoise.py` from the command line (see [Section 10.2.4.1](#) of the

*Jaguar User Manual* for details).

Do not apply the counterpoise correction if you are using LMP2 as the theoretical method.

If the complex A-B is bound by one or more hydrogen bonds, you can compute its binding energy by using Applications > Jaguar > Hydrogen Bond. This task includes the counterpoise correction. Alternatively, you can use the script `hydrogen_bond.py` from the command line (see [Section 10.2.4.2](#) of the *Jaguar User Manual* for details).

If A and B are bound by other noncovalent interactions, use M06-2X or B97-D3.

### **Reaction energies and activation barriers**

Run the geometry optimizations, transition state search, and the vibrational frequency calculations for all structures using B97-D3/6-31++G\*\*. Greater accuracy can be obtained by using a larger basis set, like cc-pVTZ(-f)+ or 6-311-3df-3pd.

### **Ionization energy and electron affinity**

Use B97-D3/cc-pVTZ(-f)++ for these calculations. Use a spin-unrestricted formalism (UDFT, not RODFT) when modeling the open-shell systems.