

Differences Between *Gaussian* Versions

This chapter presents historical descriptions of the differences between successive versions of *Gaussian* presented in reverse chronological order. The sections are taken from the corresponding versions of the *Gaussian User's Guide*, and they are presented with only minimal editing. Thus, all sections will discuss version differences using the present tense.

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Differences Between Gaussian 09 and Gaussian 03

This section briefly summarizes the major differences between Gaussian 09 and Gaussian 03. See earlier sections of the manual for full details on these features.

New Methods and Features

Energies and Derivatives

- ◆ A new implementation of recent semi-empirical models, including AM1, PM3, PM3MM, PDDG and PM6, which includes analytic first and second derivatives, user-specifiable parameters, and works with the PCM solvation models.
- ◆ TD-DFT gradients and numerical frequencies.
- ◆ Electronic excitation energies using EOM-CCSD.
- ◆ Many new DFT functionals, including the HSE, wB97, m05/m06, LC- families and the double-hybrid B2PLYP.
- ◆ Empirical dispersion models are included with the corresponding functionals.
- ◆ ROMP3, ROMP4, ROCCSD, and ROCCSD(T) energies.
- ◆ The W1RO, W1BD, and G4 compound methods for energies.
- ◆ The DFTB semi-empirical model and the DFTBA version using analytic matrix elements.

ONIOM

- ◆ ONIOM and PCM can be combined. There are several ONIOM+PCM models.
- ◆ IRCs can now be done with ONIOM, and are efficient even for molecular systems containing thousands of atoms.

Solvation

- ◆ A new algorithm for PCM solvation, which makes the energy a properly continuous function of the nuclear coordinates and which includes efficient solvation of all SCF properties. Geometry optimizations with PCM now converge at the same rate as the corresponding gas-phase optimizations.
- ◆ State-specific self-consistent solvation can be done, to model fluorescence and other emission processes.
- ◆ The SMD solvation model is available. It is parametrized to give good total solvation free energies for over a hundred solvents.

Geometry Optimizations and IRCs

- ◆ The GEDIIS geometry optimization algorithm, which is the default for minimizations. This is particularly helpful for large, floppy molecules.
- ◆ Quadratic convergence ONIOM(MO:MM) optimizations, for either mechanical or electronic embedding, and for both minima and transition structures.
- ◆ An input section can be read to control which atoms are frozen or unfrozen during an optimization. Atoms can be specified by atom, element, residue, or ONIOM layer.

Molecular Properties

- ◆ Analytic frequency-dependent ROA intensities.
- ◆ Analytic DFT hyperpolarizabilities.
- ◆ Electronic excitation, emission, and photoionization band shapes via Franck-Condon theory using harmonic normal modes for the two states.
- ◆ Electronic excitation band shapes using Herzberg-Teller or Franck-Condon-Herzberg-Teller theory.
- ◆ Normal modes can be selected for display, for anharmonic corrections, and for use in FC/HT/FC/HT analysis. Selection can be by atom, element, ONIOM layer, or residue.

Analysis and Output

- ◆ Information about protein secondary structure can be included in the molecular specification input and in.fchk files.
- ◆ Orbital by orbital population analysis can be performed, giving contributions to an orbital by atom and by angular momentum.
- ◆ Canonical UHF/UDFT orbitals can be biorthogonalization, either for visualization or for use as an initial guess for an ROHF calculation.
- ◆ Natural Transition Orbital analysis of CIS and TD excitations is available.
- ◆ Mulliken population analysis can be done after projection of the occupied orbitals onto a minimal basis. This gives stable populations when using extended basis sets.

Other New Features

- ◆ The initial guess for the SCF can be generated by combining calculations on fragments, specifying the charge and spin for each fragment.
- ◆ Numerical frequencies can be done using four-point differentiation instead of the default two-point, for better accuracy and numerical stability.

Efficiency Improvements

- ◆ HF and DFT frequencies on large molecules are much faster, especially when run in parallel.
- ◆ FMM and hence linear scaling Coulomb and Exchange are cluster-parallel.
- ◆ ONIOM(MO:MM) frequencies on large systems are much faster, especially with electronic embedding. Frequencies with 100-200 QM atoms and 6000 MM atoms are practical.
- ◆ Normal modes can be saved during large frequency calculations and reused for display or printing of modes and starting an IRC=RCFC job.
- ◆ CC, BD and EOM-CCSD amplitudes can be saved on the checkpoint file and read in to later calculations, including ones using a different basis set. BD orbitals are also saved and can be read back.
- ◆ Semi-empirical, HF, and DFT frequencies can be restarted in mid-calculation.
- ◆ CC and EOM-CC calculations can be restarted in mid-calculation.
- ◆ The initial guesses for individual steps within an ONIOM calculation can be taken from separate checkpoint files. The ONIOM=OnlyInputFiles option causes the input files for each part of the ONIOM calculation to be printed, to facilitate generating wavefunctions separately.
- ◆ The density fitting sets corresponding to the SVP, TZVP, and QZV basis sets are included. The /Fit keyword requests the fitting set matching the specified AO basis, or /Auto if there is no specific fitting set. Thus BVP86/SVP/Fit will use density fitting with the set defined to accompany the SVP basis, while BVP86/6-31G*/Fit is the same as BVP86/6-31G*/Auto.
- ◆ The DensityFit keyword can be included in the Default.Route file to make use of fitting the default whenever a pure density functional is requested.
- ◆ Density basis sets can be read in using coefficients of unnormalized primitives, density normalized primitives, or primitives normalized as though they were AOs. There are other programs which use each of these conventions, so there are published basis sets which require each of these options if they are to be read in to G09.

Functional Differences Between Gaussian 09 and Gaussian 03

- ◆ Single-point SCF calculations now default to full accuracy (SCF=Tight).
- ◆ The default integral transformation for MP, CC, and BD calculations is Tran=IABC, which is faster than Tran=Full on most machines.

- ◆ The default for Freq=ROA is CPHF=RdFreq, because the frequency-dependent ROA intensities are analytic while those in the static limit are numerical and less accurate.
- ◆ The default for post-SCF methods such as MP and CC is Tran=IABC, which is more efficient than a full transformation on most machines.
- ◆ The default SCF accuracy is SCF=Tight for all calculations, including single points.
- ◆ IRCs default to a new link, L123. Unless it is requested explicitly, the old IRC link (L115) is used only for IRCMax jobs. The default algorithm in L123 is IRC=HPC, except for ONIOM(MO:MM) calculations, for which it is IRC=EulerPC. L123 can use the IRC=GS2 algorithm (the algorithm used in L115), but this is usually much more expensive than the default.
- ◆ By default, IRCs report only the energy and reaction coordinate at each point on the path. Use IRC=Report to specify internal coordinates whose values should also be tabulated.
- ◆ Ordinary QM frequency calculations and ONIOM(MO:MM) frequencies default to CPHF=Simultaneous, as in G03. However, semi-empirical frequencies are more efficiently done using CPHF=Separate, which is the default for these cases.
- ◆ Assignment of atoms to fragments for Counterpoise and Guess=Fragment calculations or for population analysis by fragment is done in the nuclear properties part of the atom specification rather than at the end of the line, where it conflicted with ONIOM input. E.g.,

C(Fragment=3) 0.0 1.0 2.0

rather than the old format:

C 0.0 1.0 2.0 3

- ◆ Isotopes are normally specified in the nuclear properties part of the atom specification lines. If they are to be read in separately, they are read in once, after the molecule specification, rather than separately by different parts of the program (IRC, Freq, etc.).

Enhancements to Utility Programs

- ◆ The formchk utility can put additional information into the.fchk file, including user-defined MM types and other strings. This information is included when formchk is invoked with the -3 option.
- ◆ The freqchk utility can recover normal modes from the.chk or.fchk file, and can save the normal modes it generates to a.chk file (but cannot save to an.fchk file).

Summary of Changes Between Gaussian 03 and Gaussian 98

New Methods and Features

- ◆ One, two and three-dimensional periodic boundary conditions (PBC).
- ◆ Density fitting for pure DFT calculations. Support for density basis sets has been added to various basis set keywords. Density basis sets can also be generated automatically.
- ◆ Analytic molecular mechanics frequencies.
- ◆ Generalized molecular mechanics force fields and a standalone MM program.
- ◆ New SCF convergence algorithm (EDIIS + CDIIS).
- ◆ Restricted active space (RAS) CASSCF calculations.
- ◆ Analytic CCSD gradients.
- ◆ Douglas-Kroll-Hess scalar relativistic Hamiltonian (Int=DKH).

- ◆ SAC-CI energies and gradients.
- ◆ ADMP and BOMD molecular dynamics.
- ◆ Pre-resonance Raman intensities (Freq=Raman CPHF=RdFreq).
- ◆ GIAO magnetic susceptibilities (NMR).
- ◆ Spin-spin coupling constants (NMR=SpinSpin).
- ◆ Electronic circular dichroism (ECD) rotation strengths (TD).
- ◆ Vibration-rotation coupling (Freq=VibRot).
- ◆ Anharmonic vibration and vibration-rotation coupling via perturbation theory (Freq=Anharm).
- ◆ Frequency-dependent polarizabilities and hyperpolarizabilities (Polar CPHF=RdFreq).
- ◆ Hyperfine spectra tensors (Output=Pickett).
- ◆ Analytic PCM frequencies (SCRF).
- ◆ Solvent effects on vibrational spectra, NMR, and other properties and for excited states and ADMP calculations.
- ◆ ONIOM microiterations for large systems, with mechanical or electronic embedding
- ◆ Electronic embedding for ONIOM(MO:MM) calculations.
- ◆ The G3 method and variations (G3).
- ◆ The W1 method and a variation (see W1U).
- ◆ The CIS(D) excited states method.
- ◆ The extended Huckel method is now available (Huckel).
- ◆ NBO orbitals can now be saved for later use in visualization programs and subsequent jobs such as CASSCF calculations (Pop=SaveNBOs).
- ◆ Additional DFT functionals: OPTX, PBE, B95, B1, B98, B97-1, B97-2, VSXC, HCTH
- ◆ Additional basis sets: UGBS, MTSmall, DGDZVP, DGTZVP
- ◆ Additional frozen core options are now available (see FC).

Efficiency Improvements

- ◆ The FMM facility is now automated and does not need to be enabled by the user.
- ◆ O(N) exact exchange for Hartree-Fock and hybrid DFT.
- ◆ CASSCF active spaces of up to 14 orbitals for energies and optimizations.
- ◆ Quadratic coupled algorithm and microiterations for ONIOM(MO:MM) optimizations.
- ◆ Coulomb engine for pure DFT calculations.
- ◆ Guess=Read works with ONIOM and Counterpoise.
- ◆ Enhanced PCM facility (SCRF).

Functional Differences Between Gaussian 03 and Gaussian 98

- ◆ The default initial guess has changed to use the Harris guess (see Guess).
- ◆ Fundamental physical constants have been updated to the latest values (see Constants).
- ◆ Both SCRF and SCRF=PCM now default to SCRF=IEFPCM.
- ◆ Isotopes are now specified as part of the molecule specification.
- ◆ The temperature, pressure and frequency scale factor for thermochemistry analysis are now specified using the Temperature, Pressure and Scale keywords.
- ◆ By default, the orbitals displayed during population analysis after semi-empirical calculations are the orbitals resulting directly from the calculation. In Gaussian 98, these were considered to be orbitals over symmetrically orthogonalized AOs and converted back to AOs (multiplying by $S^{-1/2}$) before display. IOP(4/24=1) can be used to request the previous treatment.

Changes Introduced in Late Revisions of Gaussian 98

- ◆ CBS extrapolation uses localization based on populations in minimal basis as the default scheme (see CBSExtrapolate).
- ◆ The CBS-4 model chemistry has also been updated with both the new localization procedure and improved empirical parameters. The keyword name has changed to CBS-4M to reflect this change.
- ◆ Counterpoise calculations are now performed with the Counterpoise keyword.

Enhancements to Utility Programs

- ◆ All parameters required by freqchk can now be specified on the command line.
- ◆ chkchk -p can be used to generate data for an input file (structure, basis, MOs, etc.) from the checkpoint file.
- ◆ newzmat now provides support for fractional coordinates for crystal structures.

Summary of Changes Between *Gaussian 98* and *Gaussian 94*

New Methods and Features

- ◆ Vibrational circular dichroism intensities.
- ◆ MP2 and DFT Raman intensities.
- ◆ Enhanced version of the Polarized Continuum (overlapping spheres) model (PCM) of Tomasi and coworkers for SCRF solvent effects.
- ◆ Trajectory calculations.
- ◆ Reaction path optimizations.
- ◆ The ONIOM facility of Morokuma and coworkers.
- ◆ ZINDO and TD excited state energies.
- ◆ The IRCMax method for locating/optimizing transition states.
- ◆ Molecular mechanics methods using the AMBER, DREIDING and UFF force fields.
- ◆ Additional DFT functionals:
 - ◆ Exchange functionals: Perdew-Wang 91, Barone's modification of PW91 and Gill 96.

- ◆ Correlation functional: Becke 96.
- ◆ Hybrid functionals: Becke's 1996 one-parameter hybrid functional and with several variations due to Barone and Adamo.
- ◆ NMR calculations at the MP2 level.
- ◆ **ModRedundant** style changes to the geometry in the input stream are now permitted via **Geom=ModRedundant**.
- ◆ Forces, optimizations and frequencies with background point charges.
- ◆ Analytic ECP second derivatives.
- ◆ Transparent handling of linear dependencies in basis sets.
- ◆ Very general choices for internal coordinates in geometry optimizations.
- ◆ Additional basis sets: Davidson's modified cc-pDVZ, Stuttgart/Dresden ECP's, MIDI!, Ahlrich's SV, SVP and TZV basis sets, extended atom range for the Stevens/Basch/Krauss ECP pseudopotential and basis set.

Efficiency Improvements

- ◆ CASSCF calculations may now use an active space of up to 12 orbitals. CASSCF calculations may now use Davidson diagonalization in addition to Lanczos and full diagonalization.
- ◆ MP2 frequencies require less disk and obey **MaxDisk** more often.
- ◆ DFT frequencies speed improvements.
- ◆ Improved efficiency of parallel Hartree-Fock and DFT calculations.
- ◆ Linearly-scaling performance for large semi-empirical and DFT calculations via the fast multipole method (FMM) and sparse matrix techniques.

Functional Differences Between *Gaussian 98* and *Gaussian 94*

- ◆ The default memory amount in G98 is 6MW.
- ◆ **Opt=QST2** and **QST3** input now require a set of redundant internal coordinate modifications following each geometry specification when the **ModRedundant** option is also specified.
- ◆ The syntax for specifying modifications to redundant internal coordinates has been enhanced.
- ◆ The PCM method in *Gaussian 94* has been replaced by the code of Tomasi and coworkers. The previous facility is deprecated, but it may be accessed for retrospective comparative purposes using the **SCRF=OldPCM** keyword.
- ◆ The new **SCF=FON** facility is the default procedure.
- ◆ The **Charge** keyword now respects the units set by the **Units** keyword.
- ◆ Charges are now specified in the input orientation.
- ◆ Stratmann-Scuseria weights are the default for DFT integration.
- ◆ The cc-pV*Z basis sets have had duplicate functions removed and have been rotated in order to increase computational efficiency. As so altered, they produce identical energetic results to the cc* basis sets in *Gaussian 94*, but they no longer match those made available on the world wide web by Dunning and coworkers.
- ◆ MP3, MP4, QCISD, CCSD, QCISD(T), and CCSD(T) calculations all now look at **Maxdisk**. It is *crucial* for a value for **MaxDisk** to be specified explicitly for these types of jobs, either within the route section or via a system wide setting in the **Default.Route** file. If **MaxDisk** is left unset, the program now assumes that disk is abundant and performs a full transformation by default, in contrast to *Gaussian 94* where a partial transformation was the default in such cases. If **MaxDisk** is not set and sufficient disk space is not available for a full transformation, the job will fail (where it may have worked in G94).

Summary of Changes Between *Gaussian 94* and *Gaussian 92/DFT*

This section describes the differences between *Gaussian 94* and the two preceding releases: *Gaussian 92* and the interim-pre-release *Gaussian 92/DFT*. Note that *Gaussian 92/DFT* differs from *Gaussian 92* only in adding Density Functional Theory (DFT) methods and DFT-related features to *Gaussian 92*.

New Methods

Methods New to *Gaussian 94*

- ◆ Additional Self-Consistent Reaction Field (SCRF) methods for modeling systems in solution are available: Tomasi's method of overlapping spheres (PCM), and the IPCM model for energies at the HF and DFT levels and the SCI-PCM method for analytic energies and gradients and numerical frequencies at the HF and DFT levels.
- ◆ Automated computation of Gaussian 1 Theory, Gaussian 2 Theory, and G2(MP2) energies via a single keyword (**G1**, **G2**, **G2MP2**). Multiple step jobs are generated internally automatically, and results include free energy and enthalpy. Fast reruns with alternate temperature, pressure, and isotopes are available after job completion (as with frequency calculations).
- ◆ Automated computation of Complete Basis Set (CBS) method energies: CBS-4, CBS-q, CBS-Q, and CBS-APNO. General CBS extrapolation calculations are also available for advanced research.
- ◆ Perdew's 1991 gradient corrected correlation functional is now available.
- ◆ NMR shielding tensors may be computed with the CSGT and GIAO methods. Magnetic susceptibilities may be computed with the CGST method.
- ◆ Propagator methods (Outer Valence Green's Function) can be used to compute electron affinities and ionization potentials.
- ◆ Analytic gradients are available for the MP3 and MP4(SDQ) methods.
- ◆ Optional inclusion of MP2 correlation in CASSCF calculations.
- ◆ Functions of any angular momentum may now be used for any calculation type except AIM properties and **Complex HF** or **MP2** calculations.
- ◆ More accurate grids are now available for DFT calculations.

Methods Introduced in *Gaussian 92/DFT*

- ◆ Density Functional Theory (DFT) methods for energies, analytic gradients, and true analytic frequencies are included. Available exchange functionals are Slater (Local Spin Density), and Becke's 1988 gradient-corrected exchange functional. Available correlation functionals are the LSD correlation function of Vosko, Wilk and Nusair, functional V from the 1980 VWN paper, Lee, Yang, and Parr's gradient-corrected correlation functional, Perdew's 1981 local correlation functional, and Perdew's 1986 gradient-corrected correlation functional. The exchange functionals may be used alone or in combination with any correlation functional.
- ◆ Becke's three-parameter hybrid DFT method is available, employing either the LYP or Perdew 1986 correlation functional.
- ◆ General, user-definable hybrid models of Hartree-Fock and DFT may be specified by setting **IOp** values.

New Features

Features New to *Gaussian 94*

- ◆ Automated transition state searching using the QST method, using synchronous transit-guided quasi-Newton methods. This method uses the redundant internal coordinate method. No special Z-matrix design is needed, nor is any user-selection of variables to differentiate. A starting guess structure for the transition state may optionally be specified, but only the reactant and product structures are required.
- ◆ Analytic CI-Singles frequencies are now available for excited state systems.
- ◆ Relaxed potential energy surface scans in which a constrained geometry optimization is done at each specified point on the PES may now automatically be performed.

- ◆ The Read-Write, Integral, and D2E scratch files can be split among several distinct disk files on UNIX systems.
- ◆ CASSCF methods may be used to predict avoided crossings and conical intersections. CASSCF convergence is also improved.
- ◆ Atoms in Molecules charges, bond orders, and other properties may be computed. This feature is limited to s, p, and d functions.
- ◆ Approximate spin orbit coupling between two spin states can be computed during CASSCF calculations.
- ◆ Additional basis sets: 3-21G for third and fourth row atoms, Petersson's 6-31G† and 6-31G†† basis sets, and Dunning's cc-pV*Z correlation consistent basis sets (the double, triple, quadruple, and quintuple zeta basis sets) which may be augmented with diffuse functions.
- ◆ The Wachters-Hay all electron basis set for the first transition row has been added to the 6-311G basis set.
- ◆ Improved general basis set and ECP input: basis set specifications can refer to internally-stored basis sets to which additions can be made (see the discussion of the **Gen** keyword in chapter 3). ECP's can be specified in the same manner for **Pseudo=Read**.
- ◆ The **ExtraBasis** keyword allows additional functions to be added to internally-stored basis sets in the input file. The syntax for **Gen** and **ExtraBasis** is identical.
- ◆ The **Opt** and **Freq** keywords may be included within the same route section, and they produce an automatic two-step job where a geometry optimization is immediately followed by a frequency calculation at the optimized structure.
- ◆ The **#T** construct can be used in the route section to produce terse output which is reduced to only the essential information.

Features Introduced in *Gaussian 92/DFT*

- ◆ Stability calculations may be performed for all DFT methods.

Efficiency Improvements

- ◆ Geometry optimizations are performed by default in redundant internal coordinates, regardless of the input coordinate format. This algorithm is well-behaved even for structures exhibiting very complex bonding.
- ◆ Algorithmic improvements (dynamic formula tape generation) in CASSCF methods allow up to ten active orbitals using modest disk. In addition, the integral derivative file is no longer needed during frequency calculations, and in-core storage of the Hessian for frequencies and RFO has been removed.
- ◆ Integral-related performance improvements are present in many parts of the program.
- ◆ More intelligent use of cutoffs in the CPHF results in improved performance.
- ◆ Parallel Hartree-Fock and DFT calculations through second derivatives are possible across networks of workstations and on other non-shared memory multiprocessors, using the Linda parallel computing environment.
- ◆ Parallel performance improvements in the shared-memory parallel version.
- ◆ The **Geom=AllCheck** keyword allows the title section and charge and spin multiplicity to be retrieved from the checkpoint file in addition to the molecular structure.

Bug Fixes and Minor Changes

- ◆ The T1 diagnostic may now optionally be computed in QCISD and CCSD calculations. It is bound to the **T1Diag** option; formerly, it was available only as **IOp(9/36=1)**.
- ◆ IRC calculations now accept Cartesian coordinates for the starting molecular structure.
- ◆ When using **Guess=Read**, it is now permissible to change between pure and Cartesian functions within the basis set. For example, you may reliably use **Guess=Read** to extract the initial guess from a **HF/6-31G(d)** checkpoint file and use it for a **HF/6-311G(d)** calculation.

Functional Differences Between *Gaussian 94* and *Gaussian 92*

- ◆ Direct SCF is now the default algorithm.
- ◆ The default memory size is 4 MW.
- ◆ The redundant internal coordinates optimization procedure is now the default for geometry optimizations. The *Gaussian 92* default optimization procedure may be specified with **Opt=Z-matrix**.
- ◆ SCF calculations are now forced to maintain orbital symmetries (**SCF=Symm**).
- ◆ Specifying the cube parameters to the **Cube** keyword is now optional. If no parameters are specified other than the filename for the cube output, *Gaussian 94* will generate reasonable default values.
- ◆ In CASSCF calculations, the default Lanczos starting vector is generated differently. In *Gaussian 92*, it set C(1)=1.0. In the current program, the Lanczos starting vector is initialized in $j+1$ positions, where j is the value given to the **NRoot** option (or its default value). The positions correspond to the lowest $j+1$ energy diagonal elements of the CI Hamiltonian.

Functional Differences Between *Gaussian 94* and *Gaussian 92/DFT*

- ◆ **Int=FineGrid** is now the default.

Summary of Changes Between *Gaussian 92* and *Gaussian 90*

Here we summarize the new features in *Gaussian 92*. In order to accommodate some of the new capabilities, some minor incompatibilities in input or defaults between *Gaussian 90* and *Gaussian 92* were unavoidable.

New Methods

The major new methods appearing for the first time in *Gaussian 92* include:

- ◆ Analytical MP2 second derivatives for closed and open shell, using semi-direct methods. This allows the efficient computation of MP2 frequencies, force constants, and polarizabilities. Storage requirements are quartic (proportional to ON^3) rather than quintic as in previous analytical MP2 second derivative implementations.
- ◆ Self-Consistent Reaction Field (**SCRF**). This permits the quantum mechanical calculation to be done in the presence of a solvent. SCRF energy calculations can be performed using any method for which the analytical gradient in the gas phase is available (MP2, CI, QCISD, CCD). SCRF optimizations and frequencies can be done at the HF level.
- ◆ All correlation calculations (except complex SCF and MP2) can now be done using direct, in-core, and semi-direct methods.
- ◆ Coupled Cluster energy calculations with both single and double substitutions (**CCSD**) and with non-iterative triples (**CCSD(T)**).
- ◆ MP5 and QCISD(TQ). These are fifth-order correlation energy corrections.
- ◆ Analytical CASSCF second derivatives, allowing frequencies and force constants at that level.
- ◆ Brueckner Doubles correlation energy computations complete with triples and quadruples energy contributions: **BD**, **BD(T)**, and **BD(TQ)**.
- ◆ Fast, fully automated generation of electrostatic potential derived charges via the Merz-Singh-Kollman, CHELP, or CHELPG schemes.
- ◆ PM3 and PM3MM semi-empirical models.

New Features

- ◆ Direct and in-core GVB and CASSCF.
- ◆ AO, direct and in-core SCF stability testing. Any time a Hartree-Fock wavefunction can be generated, its stability can be tested.

- ◆ Geometry optimizations can now be performed in cartesian coordinates or in mixed internal and cartesian coordinates.
- ◆ Parallel processing of all key steps of SCF energy, gradient, and frequency calculations, and parallelization of the most costly phases of CI, MP4, QCI, CC, and BD calculations.
- ◆ CIS and correlated gradients can be done with core electrons frozen, saving disk storage, CPU and I/O time.
- ◆ Saddle points of order greater than 1 can be optimized.
- ◆ Molecular orbitals and electrostatic potentials can be evaluated over 3d grids and stored in the same format as electron densities.
- ◆ The **FormChk** utility permits generation of a formatted interface file for communication with visualization systems.
- ◆ Automatic generation of a PROAIMS/AIMPAC data file.
- ◆ Extra overlay cards in non-standard route format can be added to a standard route.
- ◆ **Skip=OvNNN** and **Skip=M** options allow further customization of a parse generated route. It is also useful in certain restarts from the RWF file.
- ◆ The defaults file can now be used to site-customize the amount of memory allocated for a *Gaussian 92* job as well as the number of processors which can be used by a single job.

Efficiency Improvements

- ◆ Prism method for direct evaluation of integrals and integral derivatives. This improves the performance of all direct and in-core calculations and all frequency calculations. It also speeds up electrostatic potential evaluation by a factor of 15-200 (depending on machine) over *Gaussian 90*.
- ◆ Direct, Semi-Direct, and Incore AO Integral Transformations. This dramatically improves the performance of methods which require or can make use of transformed integrals.

Bug Fixes and Minor Changes

- ◆ IRC calculations can now be restarted after successful termination (allowing the further specification of maxpoints).
- ◆ The temperature and pressure can now be specified for the thermochemical analysis done during frequency calculations.

Functional Differences Between *Gaussian 92* and *Gaussian 90*

Here are the known upward incompatibilities:

- ◆ Common blocks on checkpoint files has different lengths. The **C8692** utility can be used to convert *Gaussian 86*, *Gaussian 88*, and *Gaussian 90* checkpoint files to *Gaussian 92* dimensions.
- ◆ The default for all electron correlation methods is always frozen-core, since frozen-core gradients are available. **Full** must be added to correlated optimization and frequency input files from *Gaussian 90* to produce the same results in *Gaussian 92*.
- ◆ Since analytic second derivatives are available for MP2 as well as for Hartree-Fock, the CalcFC option now requests analytic second derivatives at the first point of an optimization using the specified method. It can only be used for semi-empirical, HF, and MP2 optimizations.
- ◆ The new keyword **CalcHFFC** requests analytic Hartree-Fock second derivatives as the first point of an optimization and is equivalent to the CalcFC option of *Gaussian 90*.
- ◆ **Freq=ReadIsotopes** requires different input. In *Gaussian 90*, the first line of isotope input always contained the fixed string **NO**. In *Gaussian 92*, this is replaced by a line containing the temperature (in K) and pressure (in atmospheres) to be used in the thermochemistry analysis.
- ◆ In *Gaussian 90*, either **CIS SCF=Direct** or **CIS=Direct** implied that both the SCF and CIS phases of the calculation were to be done by direct means. In *Gaussian 92*, **CIS SCF=Direct** requests direct SCF, followed by a semi-direct integral transformation, and a

CIS calculation using the MO integrals. This is a low-disk usage, high CPU efficiency combination which was not possible in *Gaussian 90*. **CIS=Direct** requests the no (quartic) disk, full direct combination, which should be used only if insufficient disk is available even for the small number of MO integrals required by MO approach.

Differences between MNDO in *Gaussian 92* and MOPAC

The code in *Gaussian 92* which implements the MINDO/3, MNDO, AM1, and PM3 Hamiltonians is a slightly modified subset of the MOPAC program of J. J. P. Stewart, version 4.0. The subset is essentially those routines from MOPAC which are required to evaluate a single point energy plus cartesian derivatives (i.e., those required if XYZ 1SCF GRADIENTS were specified on the MOPAC keyword card). The parameters used, however, are up to date and consistent with both MOPAC 6.0 and AMPAC 2.1. Most of the modifications were changes required to interface to the *Gaussian 92* style of providing input data and options and of storing intermediate results, so that the standard *Gaussian 92* geometry optimization, initial guess, and population analysis routines could work with AM1 energies, forces, and wavefunctions. The general cleanliness and high standard of programming adhered to in MOPAC made the required changes quite modest. There are some practical differences which result from these changes, however, and also a few minor bug fixes and improvements which were made:

- ◆ The PRECISE option of MOPAC is always in effect; the SCF convergence is tightened up to a level more consistent with that of the rest of *Gaussian 92*. In order to assist in achieving the tighter convergence, the *Gaussian 92* three and four point density matrix extrapolation routines have been incorporated.
- ◆ Only closed-shell RHF and UHF are supported; the CI and half-electron methods are not available not functional. Hence UHF is the default for open-shell systems.
- ◆ MOPAC allows only certain spin multiplicities, specified by keywords. Any charge and multiplicity can be specified in the usual way for the *Gaussian 92* version.
- ◆ Initial guess orbitals are generated in the standard *Gaussian 92* initial guess program, using a non-iterative extended Huckel method to avoid excessive cost. The usual route options to control the guess can be used.
- ◆ *Gaussian 92* prints molecular orbitals in the deorthogonalized basis, while MOPAC prints them in the ZDO basis. This can be overridden by setting option 24 in overlay 4 (**IOp(4/24=3)**).
- ◆ Population analysis is done using de-orthogonalized orbitals and density matrices. The resulting populations are consistent with the Mulliken populations provided by MOPAC. The deorthogonalization can be overridden by setting option 24 in overlay 4 (**IOp(4/24=3)**).
- ◆ The *Gaussian 92* minimization and transition state methods are used; none of the geometry variation methods from MOPAC are available. Consequently, the convergence criteria on optimizations are the standard *Gaussian 92* values and MOPAC features such as reaction coordinate searches (DRC keyword) and the X method of locating approximate transition states (SADDLE keyword) are not available.
- ◆ MOPAC does a geometry optimization by default and the 1SCF keyword must be specified in order to do a single SCF calculation. *Gaussian 92* defaults to a single point calculation and OPT must be specified for a geometry optimization. The FORCE keyword in MOPAC requests that force constants be computed, while in *Gaussian 92* the FORCE route keyword requests that the forces be computed. Furthermore, in MOPAC if FORCE is specified and the geometry is not optimized, an optimization is performed. Hence the equivalent of a MOPAC FORCE job is a compound job in *Gaussian 92* which does **Opt** in the first job step and **Freq** in the second. The 0SCF option in MOPAC, which just checks the input data, can be simulated in *Gaussian 92* by using the **%KJob** Link 0 command:

```
%KJob L301
```

to terminate the job after the molecule specification input has been read. In summary:

MOPAC	<i>Gaussian 92</i>
Defaults	OPT
0SCF	%KJob L301 (separate line before route card)
1SCF	Defaults
1SCF GRADIENTS	FORCE
DRC	IRC
SADDLE	OPT=TS, OPT=(EF,TS), or LST followed by OPT=TS
FORCE LET	FREQ
FORCE	OPT followed by FREQ in next job step

- ◆ Numerical differentiation of gradients to produce force constants in *Gaussian 92* takes advantage of molecular symmetry to reduce the number of SCF calculations required.

- ◆ The vibrational frequency analysis in *Gaussian 92* uses the most abundant isotopes rather than the average atomic weight.
- ◆ The usual *Gaussian 92* diagonalization routine is used instead of the routine distributed with MOPAC.
- ◆ Sparkles (± 1 and ± 2 charges without basis functions) can only be requested by giving the “atomic numbers” assigned to them; the MOPAC symbols ++, +, -- and - cannot be used. Instead, use atomic numbers 103, 104, 105, and 106, respectively.
- ◆ Lithium in *Gaussian 92* uses the MNDO parameters of Thiel rather than a +1 sparkle.
- ◆ Externally supplied parameter sets are not supported.
- ◆ Systems periodic in one dimension are not available in *Gaussian 92*.
- ◆ Other equivalents for MOPAC keywords:

MOPAC	<i>Gaussian 92</i>
PULAY	DIIS
RESTART	OPT=RESTART or FREQ=RESTART
SCFCRT	SCFCON
ITRY	SCFCYC
SPIN	Pop=Regular
SYMMETRY	Use the same variable more than once in the Z-matrix.
T	Specify a time when submitting the job, using the local batch system command
THERMO	Done by default during frequency calculations. Use Freq=ReadIso or the Browse Chemical Database System to do thermodynamics at different temperatures and pressures.
TRANS	Determined automatically by <i>Gaussian 92</i> as needed.
VECTORS	Pop=Regular or Pop=Full
S1978	AM1=S1978
Si1978	AM1=Si1978
ANALYTIC	AM1=Analytic

The **newzmat** utility, described in chapter 4, can be used to convert between MOPAC and *Gaussian 92* input files.

Summary of Changes Between *Gaussian 90* and *Gaussian 88*

New Methods

The major new methods appearing for the first time in *Gaussian 90* include:

- ◆ Direct and Semi-Direct MP2. This allows MP2 calculations to be performed using whatever amounts of disk and memory are available.
- ◆ Efficient direct SCF frequencies.
- ◆ In-core SCF (through second derivatives) and MP2, which permit extremely fast calculations when large amounts of memory are available.
- ◆ Excitation energies using CI with single excitations. This includes CIS properties and gradients (excited state structures) and direct CIS for use on large molecules.
- ◆ CASSCF is available, with gradients. The CAS-UNO method can be used to generate the initial active space.

New Features

- ◆ **Geom=Modify** permits the reading in of optimized parameters off the checkpoint file combined with altering frozen variables from the previous calculation. This facilitates partial optimizations and permits relaxed potential surface scans to be performed. Variables can be altered, frozen, and unfrozen individually. Use of frozen variables with **geom=checkpoint** works as expected.
- ◆ All generalized and excited state densities can be recovered from the checkpoint file and analyzed without repeating compute-intensive calculations.

- ◆ The alpha, beta, and spin densities can now be used instead of the total density in multipole and electrostatic potential analysis.
- ◆ Natural orbitals can be generated from any density.
- ◆ The Reed and Weinhold Natural Bond Orbital analysis program has been incorporated.
- ◆ Direct SCF is now restartable, as is direct CIS.
- ◆ Intrinsic Reaction Coordinates can now be following in internal, cartesian, or mass-weighted coordinates.

Efficiency Improvements

Numerous performance improvements have been made. The changes include:

- ◆ In addition to reducing disk usage, the new semi-direct MP2 algorithms make all MP2 and MP2 gradient calculations significantly faster.
- ◆ QCISD is now faster and the extrapolation (convergence acceleration) procedure is much more reliable.
- ◆ **NORAMAN** option to skip computation of Raman intensities during frequency and **Opt=CalcAll** jobs.
- ◆ Direct SCF has been sped up significantly. Direct SCF single points, for which only the density and energy are sought, are sped up even further.
- ◆ Frequency calculations have been sped up by improvements in both the CPHF (L1002) and integral derivative (L1110) steps.
- ◆ CI gradients have been sped up by improvements in the back-transformation of the two-particle density matrix (L1111).
- ◆ Machine-dependent routines are available to accelerate integral transformations and SCF calculations using regular integrals.

Bug Fixes and Minor Changes

These changes include responses to bug reports and requests based on previous versions of the program.

- ◆ Problems with estimation of force constants for atoms heavier than Argon and for systems with 3 or more collinear atoms have been fixed.
- ◆ Archive entries can be recreated from the checkpoint file.
- ◆ Routines FILEIO and ILSW are now machine-independent.

Functional Differences Between *Gaussian 88* and *Gaussian 90*

In the interests of generality and efficiency, a few changes have had to be made in the default behavior of *Gaussian 90*.

- ◆ **SCF Convergence:** In *Gaussian 90*, the default SCF convergence is 10^{-4} for single-point direct SCF calculations. This is adequate accuracy for those properties which are usually produced from single-point calculations (populations, electrostatic potentials, SCF energy, dipole moment, etc.) and requires only half the CPU time of a fully converged calculation. The tight convergence for single points can be restored by specifying **SCF=Tight**. Non-direct single-point calculations and direct calculations other than SCF single points continue to use tight (10^{-8}) convergence.
- ◆ **QCISD vs. QCISD(T):** In *Gaussian 88*, the triples correction was always included in QCI calculations, reflecting an expectation that QCISD would be used primarily in single point energy calculations. *Gaussian 90* includes the analytic gradient of the QCISD energy, making geometry optimizations practical, so it is necessary to distinguish which method (**QCISD** or **QCISD(T)**) is desired. Accordingly, there are now distinct keywords for the two models.

Several defaults and convergence criteria have been changed in *Gaussian 90*. These changes produce increased performance but should not affect results.

- ◆ The default SCF convergence has been reduced from 10^{-9} to 10^{-8} .

- ◆ The default CPHF convergence has been reduced from 10^{-9} to 10^{-8} .
- ◆ CPHF solution is done simultaneously rather than separately by default.
- ◆ Link 502 is used for the SCF phase of all RHF, ROHF, and UHF calculations.
- ◆ QCISD optimizations default to full rather than frozen-core, so that analytic gradients can be used.
- ◆ The functionality in Link 903 (MP2 without storing transformed integrals) is included in Link 906 (direct MP2), so Link 903 has been omitted.
- ◆ Links 304, 312, 505, and 903, which were included in *Gaussian 88* but which do not add any functionality, have been omitted from *Gaussian 90*.
- ◆ MP2 calculations use the new and faster semi-direct algorithms. As a result, the wavefunction is not saved on disk and the density correct to second order is not computed. The correct MP2 density is of course still computed. The old MP2 code can be requested via **MP2=NoDirect**.

Summary of Changes Between *Gaussian 88* and *Gaussian 86*

New Methods

The major new features appearing for the first time in *Gaussian 88* include:

- ◆ An eigenvalue-following (mode-walking) optimization method is available.
- ◆ This uses Baker's implementation of Simon's method. The method can take as input either energies, energies and gradients, or energies and gradients and second derivatives. Both minima and transition states can be located, although the primary purpose of the method is in walking uphill to transition states.
- ◆ The reaction path following (intrinsic reaction coordinate) algorithm of Gonzalez and Schlegel can be used to explore the paths down from a transition state to reactants and products.
- ◆ Effective core potentials (ECPs) can now be used. ECP gradients are also available.
- ◆ Quadratic convergence SCF, which combines quadratic (Newton-Raphson) steps with linear searches, is available as an alternative for systems which fail to converge using the conventional SCF methods.
- ◆ Direct SCF. This permits recomputation of the two-electron integrals on each SCF iteration, thereby avoiding the need for $O(N^4)$ external storage. Both conventional and quadratic SCF procedures can be used with the direct method. Optimizations and analytic second derivatives can also be computed without external storage of integrals.
- ◆ The Quadratic Configuration Interaction model is available.
- ◆ The Møller-Plesset energies after projection of multiple spin contaminants are computed for open-shell systems.
- ◆ Polarizabilities and hyperpolarizabilities can be computed for correlated energies, using numerical differentiation of energies and dipole moments.
- ◆ The electron density can be evaluated over a grid of points, for plotting and other analysis.
- ◆ Densities including the effects of electron correlation, defined as the response of the correlated energy to any one-electron perturbation, can be computed. These can be used for population analysis, plotting, and electrostatic properties.
- ◆ Automatic updating of a database containing the key results of calculations performed using *Gaussian 88* is available, in conjunction with the Browse Quantum Chemistry Database System (available separately). Full CI calculations can be done.

New Features

Many features have been added, for the most part directed towards either (a) finer control of some of the algorithms in *Gaussian 88*, (b)

to assist in the handling of difficult cases, or (c) to provide additional information already available at the end of a calculation. These include:

- ◆ *Gaussian 88* can handle up to 2000 shells of basis functions. While this is more than is likely to be practical for a while, the previous limitation of 200 shells effectively imposed by the initial guess and some integral programs has been lifted
- ◆ The electrostatic energy terms (kinetic energy, potential energy, etc.) from the SCF wavefunction are printed along with the population analysis.
- ◆ Optional replication of two-electron integrals using symmetry during SCF processing. This permits use of the petite integral list with wavefunctions which do not have the full molecular symmetry.
- ◆ DIIS and BFGS extrapolation of CI, QCI and CCD iteration has been added.
- ◆ It is possible to repeat the vibrational frequency analysis following a frequency calculation using information stored on the checkpoint file. The isotopes used in the analysis can be specified.
- ◆ A bonding population analysis (i.e., involving only interatomic density terms) can be performed.
- ◆ A final SCF cycle is performed after convergence without extrapolation or recursive Fock matrix formation. This can be suppressed for intrinsically divergent cases.
- ◆ All available densities (i.e., both SCF and correlated) are stored permanently, for use by other programs.
- ◆ Successive partial and full optimizations can be done without loss of Hessian information.
- ◆ The AM1 method has been updated to be consistent with MOPAC version 4.0. Old sulphur and silicon parameters and analytic derivatives are now available via standard routes.
- ◆ The *newzmat* input generator can symmetrize coordinates and thus generate proper symmetry-constrained Z-matrices from “almost” symmetric coordinates. It can also handle input to and output from checkpoint files and both unformatted and formatted MacroModel version 1.5 files.
- ◆ *ham506* now generates the correct Hamiltonians for separate orbitals as required by Link 506.

Efficiency Improvements

Numerous performance improvements have been made. SCF gradients, SCF second derivatives, and post-SCF gradients have all been sped up significantly. The changes include:

- ◆ Reduced AO integral file i/o during integral transformation when memory is plentiful.
- ◆ Improved second, third, and fourth quarter integral transformations.
- ◆ Convergence of restricted open-shell SCF has been improved, thanks to a suggestion of John Montgomery.
- ◆ When the AO integrals fit in one or two integral buffers, these are read only once during the SCF. Thus by increasing the integral buffer size sufficiently, in-core SCF calculations can be done.
- ◆ Simultaneous CPHF solution is now the default for Opt=CalcFC, since only modest accuracy in the computed force constants is needed to start an optimization.
- ◆ First order electric field CPHF is done only once during frequency calculations, and second-order electric field CPHF is no longer needed for the polarizability derivatives. Thus a total of 9 CPHF solutions are avoided in every frequency calculation.
- ◆ Post-SCF gradient calculations no longer involve writing out the integral derivatives. Handy’s interchange (“Z-vector”) method is used to reduce the number of CPHF solutions required from 3 x number of atoms to 1.
- ◆ Special SP code has been added for two-electron integral second derivatives, considerably speeding up STO-3G and 3-21G frequencies.
- ◆ The new Head-Gordon/Pople algorithm is used for all integral derivatives on the Trace and for integral derivatives involving d functions on the VAX. This is noticeably faster for 6-31G* gradients on the VAX than the old Rys code, and dramatically faster

for all basis sets on the Trace.

- ◆ A new method for approximating the initial Hessian in geometry optimizations based on a valence force field is now used. This provides a much more reasonable Hessian for ring-containing systems than the previous diagonal guess.
- ◆ All code for CI and QCI calculations has been merged into one link, thereby greatly reducing the overhead and elapsed time in these cases.
- ◆ The atomic-orbital basis CPHF code has been streamlined.

Bug Fixes and Minor Changes

These changes include responses to bug reports and requests based on previous versions of the program.

- ◆ AM1 optimizations now provide a population analysis at the final geometry, as in ab initio optimizations.
- ◆ **NRSscale** is now the default for transition state optimizations.
- ◆ The maximum allowed molecular orbital coefficient during post-SCF calculations is 1000 instead of 100. This limit can still be over-ridden with the **NoTestMO** keyword.
- ◆ The check for linear independence of geometrical variables requested by the **FOPT** keyword is now fast enough to use routinely.
- ◆ Problems with the symmetry orientation changing during optimizations have been resolved.
- ◆ The atomic charges resulting from the Mulliken population analysis are stored on the checkpoint file for use by other programs.
- ◆ Masses are now stored for all elements, removing problems with frequency analysis for systems containing third-row or heavier atoms.
- ◆ The physical constants used to convert from atomic units have been updated with the latest values. Note that these differ more than expected from previous values. The old constants are still available for compatibility with previous versions of the *Gaussian* system.
- ◆ Various difficulties with exceeding 100 atoms and about 200 shells have been resolved.
- ◆ An option to produce an input file for the GAMESS program has been added.
- ◆ **Guess=Translate** is now the default for **Guess=Read**. This is the correct default for the common case of reading in a guess from one geometry to use at another geometry of the same molecule. For example, it avoids problems with using a wavefunction for two atoms at long distance as a guess for diatomic. If a guess is read in for a system having a different stoichiometry (i.e., a wavefunction for a H₂CO read in for H₂CN⁺), then **Guess=NoTranslate** must be specified.
- ◆ The integral file can be deleted after the transformation, relieving disk space limitations in large MP2 calculations.
- ◆ The density matrix expanded to second order in the Møller-Plesset parameter can be computed. Note that this is not the same as the MP2 density defined as a response function.
- ◆ The one-particle density matrix corresponding to the CI wavefunction can be computed. Note that this is not the same as the CI density defined as a response function.
- ◆ A utility program, **c8688**, has been provided to convert checkpoint files from *Gaussian 86* to *Gaussian 88* format. This permits **Guess=Read**, **Geom=Check**, and **Opt=ReadFC** from old checkpoint files. An optimization begun with *Gaussian 86* cannot be restarted in *Gaussian 88*, although a new optimization can be started using the above three options.
- ◆ On the VAX, the problem with large group numbers has been fixed. Shareable images are no longer used, since the memory limitations which lead to their introduction are no longer common. The directory structure used to hold the program has been simplified.
- ◆ On the Trace, default routes and memory sizes smaller than 1,000,000 words now work. The total CPU time and final file sizes are printed at the end of each job step. Asynchronous I/O is used. Input and output file names can be given on the command line. Scripts are provided to facilitate the use of *Gaussian 88* with the NQS batch system.

Summary of Changes Between *Gaussian 86* and *Gaussian 82*

New Methods

- ◆ Several semiempirical models are now available in *Gaussian 86*. These include the original CNDO/2 and INDO methods and the more recent MINDO3, MNDO and AM1 approaches. The latter three are provided by a subset of the MOPAC program of J. J. P. Stewart. AM1 is generally the most reliable of these methods for predicting structures and vibrational frequencies. Force constants from the AM1 method can be generated for use in the initial Hessian of ab initio geometry optimizations.
- ◆ The Linear Synchronous Transit method of Halgren and Lipscomb is now available for locating initial starting guesses for transition state optimization.
- ◆ Restricted high spin open shell Hartree-Fock (ROHF) is now available in an efficient implementation, including DIIS extrapolation and analytic gradients.
- ◆ The Generalized Valence Bond-Perfect Pairing method is provided by a modified version of the F. W. Bobrowicz program GVBTwo. Gradients are available.
- ◆ Dipole, quadrupole, octapole, hexadecapole, and Fermi contact terms can be added as a perturbation to the one-electron Hamiltonian. An arbitrary point charge distribution can also be added to single-point calculations to simulate crystal or solvent fields.
- ◆ The intensities of both infrared and Raman transitions are now predicted along with the frequencies.
- ◆ Dipole polarizabilities and hyperpolarizabilities can now be computed analytically, and are included automatically in frequency calculations. Numerical calculation of MP2 or CI polarizabilities is also available.
- ◆ Several new output options have been added to ease communication with other programs:
- ◆ An input deck for one flavor of the HONDO/GAMESS system can be punched. The deck (or the code to generate it) is easily modified for most other variants.
- ◆ The MO's can be punched in addition to the atomic and other information available in *Gaussian 82*.
- ◆ The IntGenF, PolyAtom, and Tran2P5 binary files used by the Caltech system of programs can be generated.
- ◆ With a few minor exceptions, all arrays whose size depends on the number of basis functions are now dynamically allocated, removing all restrictions on number of functions other than integral packing limitations and budget. Other dimensioning limits have been increased substantially and made more consistent. For example, the program is now dimensioned for 400 atoms, 400 Z-Matrix cards, and 1200 Z-Matrix variables.
- ◆ The Z-matrix has been extended to include cartesian coordinates as a special case, and to allow for the specification of fixed atoms whose cartesian derivatives need not be computed (for example, in chemisorption studies).

Efficiency Improvements

- ◆ The route generator has been made more flexible, both to allow local customization for production runs and to facilitate debugging.
- ◆ A customization file can override the programs internal defaults for many route options.
- ◆ A command has been added to specify non-standard values for internal options within standard routes.
- ◆ Additional links can be included in otherwise standard routes.
- ◆ The **FOpt** (Full Optimization) is identical to **Opt** but in addition requests a check that the specified Z-matrix variables are both linearly independent and exactly equal in number to the number of degrees of freedom in the molecule.
- ◆ The Berny optimization algorithm has been made considerably more robust, especially for strained systems. It now uses a variable trust-radius to handle large steps and scale excessive step using a variant of the method of Simons. See the discussion of the **Opt** keyword chapter 3 for complete description of the algorithm. By default, the Hessian is only printed at each step if 20 or fewer variables are involved, to avoid $O(N^2)$ printed output.

- ◆ A simple optimization algorithm which does straight Newton-Raphson iterations using a fixed read-in Hessian and numerically computed gradients has been added. This is useful for refining MP2 into MP4 transition states, etc.
- ◆ The Berny optimizer can now start with a unit Hessian. This is preferable for highly strained systems for which the standard estimate of the Hessian is inaccurate.
- ◆ The **Opt=MNDOFC** suboption computes an initial Hessian using the MNDO (actually AM1) method. This is beneficial for highly strained systems as well as for molecules specified by unusual Z-matrices (i.e., having many dummy atoms).
- ◆ Numerical differentiation with respect to dipole fields and Fermi contact perturbations has been added. The former is used to compute post-SCF dipole moments, infrared intensities and polarizabilities while the latter is useful for post-SCF computation of hyperfine interactions.
- ◆ Vibrational frequencies can now be computed via double numerical differentiation, as can Hartree-Fock third derivatives.
- ◆ A multitude of additional basis sets have been added to the program and the input format for general basis sets has been greatly streamlined. These include Dunning's contraction of Huizinaga's primitive sets for first and second row systems, and the addition of MacLean and Chandler's second row extended basis sets for use with the 6-311G first row basis.
- ◆ General basis set input has been made free-format, simplified, and made more appropriate for maintaining libraries of basis sets. Basis set information can be read from the checkpoint file to facilitate compound jobs with general basis sets. Standard basis sets can be printed in general basis format to facilitate modifications of standard bases.
- ◆ All standard integral and integral derivative programs now handle through f functions.
- ◆ Integral first derivatives need no longer be written out for Hartree-Fock frequency calculations; they are summed directly into the appropriate Fock matrix derivatives.
- ◆ Pulay's Direct Inversion in the Iterative Subspace (DIIS) method is now available for closed and open shell SCF.
- ◆ Virtual level shifting is also available as an aid in convergence.
- ◆ ROHF calculations now use the method of McWheeny along with DIIS extrapolation.
- ◆ The CPHF link has been provided with several new strategies. The CPHF equations can be solved in the AO as well as the MO basis. The default for HF frequencies is to use the AO basis and store only the symmetry unique integrals ("petite list") on disk. This is noticeably slower than MO solution, especially for very large molecules in which the $O(N^5)$ CPHF solution dominates the $O(N^4)$ integral second derivatives, but it minimizes the disk storage required. CPHF can be solved for general perturbations. A uniform electric field (i.e., dipole perturbation) as well as nuclear coordinate displacements are routinely included. Second as well as first order CPHF can be done. This is the method employed in determination of polarizability derivatives. The CPHF equations can be solved using a single expansion space for all variables. This is faster but presents numerical instabilities and hence is not the default.