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COMMISSION ON MOLECULAR STRUCTURE AND SPECTROSCOPY*
SUBCOMMITTEE ON THEORETICAL CHEMISTRY**

GUIDELINES FOR PRESENTATION OF METHODOLOGICAL CHOICES IN THE PUBLICATION OF COMPUTATIONAL RESULTS

A. AB INITIO ELECTRONIC STRUCTURE CALCULATIONS

(IUPAC Recommendations 1998)

Prepared for publication by
James E. Boggs

Department of Chemistry, The University of Texas, Austin, Texas 78712

**Membership of the Subcommittee on Theoretical Chemistry during the preparation of this report was as follows:

Chairman: J. E. Boggs (U.S.A), George Famini (U.S.A.), R. Janoschek (Austria), Z. B. Maksic (Croatia), I. M. Mills (U.K.), P. v. R. Schleyer (Germany), J. J. P. Stewart (U.S.A.).

*Membership of the Commission during the preparation of this report (1995-97) was as follows:

Chairman: J. E. Bertie (Canada); *Secretary*: P. Klaeboe (Norway); *Titular Members*: T. Janoschek (Austria); B. P. Winnewisser (Germany); S. Tsuchiya (Japan); A. M. Heyns (RSA); J. E. Boggs (USA); *Associate Members*: S. M. Cabral de Menezes (Brazil); C. Zhang (China); E. Hirota (Japan); A. Oskam (Netherlands); *National Representatives*: J. E. Collin (Belgium); S. Califano (Italy); J. J. C. Teixeira-Dias (Portugal); Y. S. Lee (Republic of Korea); D. Escolar (Spain); J. Kowalewski (Sweden); S. Suzer (Turkey); R. K. Harris (UK).

Guidelines for Presentation of Methodological Choices in the Publication of Computational Results
A. Ab Initio Electronic Structure Calculations

James E. Boggs

Synopsis: **Guidelines are presented to assist authors in preparing manuscripts that describe the results of ab initio computation. These guidelines are not intended to recommend how ab initio calculations should be done, but rather to ensure that the reader can have a clear understanding of what actually was done. They are written in a form to facilitate reprinting in original research journals and as information sheets that can be distributed to authors and reviewers.**

Basic Principles

The basic principles are the same as for all scientific publication:

(1) Enough information should be given to enable the reader to repeat the calculation. This is the overall guiding principle of these recommendations.

(2) Credit should be given for all work taken from others.

(3) Care and courtesy should be exercised and complete references given if comparisons are made to other computational or experimental work.

(4) Acronyms should be used only when they increase the readability of a paper. All but the most common should be written out at first use.

(5) Reporting an excessive number of figures in computed parameters should be avoided. In general, show only the number which can be anticipated to be meaningful in comparison with reality. If digits which are not significant are quoted to facilitate exact reproduction of the calculation, indicate this fact.

Use of commercial or other widely distributed programs

(1) Identify the program, providing a literature reference and the version number, if any.

(2) If the method uses a basis set, it must be specified with precision or reference made to a publication where it is fully specified. Specification of a basis set requires listing of exponents, contraction coefficients and the number of functions in a subshell (e.g., 5 or 6 d functions, 7 or 10 f functions).

  (a) Use a slash to separate the electronic model from the basis set, such as RHF/3-21G or MP2/6-31G**. Use a double slash if the model used for a subsequent single point calculation differs from the model used for geometry optimization, such as MP2/6-31G**//RHF/3-21G*. The method for the single point calculation should come before the //.

  (b) The source of the basis set must be given. The original reference should be cited. If the numerical values of the parameters in the basis set are not given in the cited published reference, they should be listed in an appendix or in a permanently available archive. Reference to a basis set as implemented in a specific program is discouraged since such a reference may not be available to future readers. Also note that some programs use different parameters for a given basis set than originally proposed; the 4-21 basis set as implemented in Gaussian-94, as one example, is different from that proposed by the original authors and used in some other programs.

  (c) The form "Dunning's cc-pVDZ" with a reference is satisfactory if the reference describes the basis fully. Note that the acronym should be written out the first time it is used. Alternatively, the nomenclature “(15s9p2d1f/10s5p2d1f/5s2p1d) contracted to [5s4p2d1f/4s3p2d1f/3s2p1d]” with a reference listing the contracted and uncontracted basis sets is satisfactory.

(3) If a post-Hartree-Fock method is used, identify it fully.
   (a) If the version used is embedded in a program package, give that reference. If not, give a reference to the source from which it was obtained. In either case, refer to the original authors if possible. Be generous in acknowledging the contributions of others.
   (b) Describe all options chosen; e.g., are all electrons correlated or only valence electrons? Remember that the information given should enable the reader to reproduce the work and get the same numerical result.
   (c) If a multiconfiguration reference state was used, make clear which configurations were selected or how they were selected.
(4) Other methodological choices must be specified.
   (a) In some cases there is a well established notation to indicate further restrictions to an electronic model, e.g., MP2(FC) indicates a frozen core in an MP2 calculation. When such a convention does not exist, use an underscore. For example, use MP2_PP to indicate a pseudopotential or MP2_ECP to indicate an effective core potential. Such acronyms should be identified when first used and details of the approximations must be given or a reference cited.
   (b) If relativistic corrections were used for heavy atoms, specify the method precisely, with references.
   (c) If an unrestricted Hartree-Fock calculation was used, give the value of the S^2 operator before and after annihilation.
(5) Specify the method of convergence (level shifting, DIIS, conjugate gradients, etc) if it is not the default option in the program used or if convergence was hard to attain.

Use of an original program for either the basic calculation or for analysis of the results

(1) The theory should be given in sufficient detail that the reader could, at least in principle, write a program to do the same thing. If the method has already been completely described in the open literature, a reference will suffice. Note that hope of future commercialization is not an adequate reason for withholding details of what was done. The program developer cannot have it both ways — if it is desired to publish results in the open, refereed scientific literature, full disclosure should be demanded by the editor and reviewers.
(2) If the new program is available from the author, the conditions under which this is possible should be given. Note that some journals require such availability as a condition for publication.

Geometry optimization or vibrational calculations

(1) Report any geometry constraints that were used. If the starting geometry was symmetric, identify that symmetry.
(2) Quote the convergence limit used for geometry optimization if it is different from the default value of the program. Report efforts, if any, to locate and identify the global minimum.
(3) If force constants are reported, give their units and make sure the vibrational coordinates being used are clear. If internal coordinates are used, they must be clearly defined since internal coordinates are not unique, even symmetrized ones. If not included in the publication, the force field and intensities in Cartesian coordinates should be submitted as a supplementary publication. Identify the geometry at which the force constants are evaluated, and if Cartesian force constants are given, be sure to give the Cartesian atomic positions on which they are based.

Transition structures in chemical reactions

(1) Specify whether frequency calculations have confirmed that one and only one imaginary frequency exists. Give its magnitude and the lowest real frequency.
(2) Specify whether explicit calculations have identified the stationary points linked by the transition structure.

Molecular properties

(1) Report the method of calculation of quantities such as dipole moment, polarizabilities, shielding tensors, etc. Give a reference to the original sources.
(2) For origin-dependent molecular properties, the origin of the corresponding generators should be clearly specified.
(3) If prinicpal values are reported for tensor quantities, the specification of the principal axes is recommended, possibly as supplementary material.

Use of density functional theory

(1) Identify the exchange functional and correlation functional used, with references.
(2) Specify the basis set as described above.
(3) If a combination method is used, specify it fully with a reference.

Comparison with experimental data

(1) Give a reference to the original source of the data. If you use a data compilation, that reference may be helpful, but be sure to check the original references to verify the accuracy of the numbers cited and to note any relevant comments in the text, such as expected error limits or assumed parameters.
(2) Specify the nature of the experimental data with which comparison is made. Giving an experimental bond length, for example, is not meaningful unless the type of measurement and analysis are also given. X-ray diffraction measures the distance between centroids of electron density while electron or neutron diffraction measure the distance between nuclei. Electron diffraction may yield a vibrationally averaged distance while microwave spectroscopy may produce anything from an equilibrium distance (the only experimental parameter directly comparable to a computationally optimized internuclear distance) to a purely operationally defined substitution distance. Symbolism such as r_g, r_s, r_e is fine, accompanied by a reference defining these quantities. Distinguish between observed and harmonic wavenumbers.
(3) If the original author gives an estimated uncertainty such as 154.2(7) nm, quote the uncertainty as part of the experimental data. It is, of course, proper to make an informed judgment as to the reasonableness of the estimate.
(4) Avoid vague statements such as "good agreement". A comparison such as "agreement within the estimated experimental uncertainty" or "within twice the experimental uncertainty" has clear meaning.
(5) Make proper distinction between the concepts of wavenumber and of frequency.

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