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Quantum Mechanical Calculations to Chemical Accuracy

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Full configuration-interaction (FCI) calculations have given an unambiguous standard by which the accuracy of theoretical approaches of incorporating electron correlation into molecular structure calculations can be judged. In addition, improvements in vectorization of programs, computer technology, and algorithms now permit a systematic study of the convergence of the atomic orbital (or so-called one-particle) basis set. These advances are discussed and some examples of the solution of chemical problems by quantum mechanical calculations are given to illustrate the accuracy of current techniques.

THE YEAR 1970 HAS BEEN CITED (*1*) AS THE STARTING DATE for the "third age of quantum chemistry," as theory began obtaining quantitative solutions to chemical problems. Since that time, the number of problems for which theory has contributed has grown dramatically. See, for example, the review by Schaefer (*1*) where the success of theory is demonstrated on problems ranging from aiding in the identification of interstellar microwave lines to the prediction of ground-state structures, such as the $^3B_1$ state of CH_2. We contend that another large enhancement in the utility of theory for solving chemical problems occurred in about 1987, as a result of benchmark calculations that considerably enhanced our understanding of the fundamental approximations used in standard quantum mechanical approaches (*2*). This led to the observation that the largest shortcoming of the theoretical treatment was often the incompleteness of the atomic orbital (AO) basis, as opposed to limitations in the treatment of electron correlation.

In this review, we present several examples of theoretical calculations that illustrate the accuracy of present-day molecular structure calculations. It is, of course, impossible to describe all of the approaches in use today. Instead we limit the discussion to two approaches. First is the coupled-cluster singles and doubles (CCSD) method (*3*) with a perturbational estimate (*4*) of the contribution of connected triple excitations [CCSD(T)]. Because the FCI method (5–7) is not feasible for most systems, this is probably the most accurate, practical single-reference approach in use today. Second, we consider the multireference configuration-interaction (MRCI) approach to the correlation problem. Size-extensive modifications, such as the averaged-coupled pair functional (ACPF) approach (*8*), further extend the applicability of the MRCI approach. Multireference correlation treatments are generally the most accurate approaches, because they account for both dynamical and nondynamical correlation. These approaches have been shown (*2*) to reproduce FCI results for both the energy and molecular properties for a wide range of molecular systems.

New Insight from Benchmark Calculations

Most quantum mechanical methods attempt to solve the time-independent Schrödinger equation

$$\hat{H}\Psi = E\Psi \tag{1}$$

where Ψ is the wave function, E is the energy, and $\hat{H}$ is the Hamiltonian. Because the electrons are much lighter than the nuclei, the electronic and nuclear motions are generally treated separately (the Born-Oppenheimer approximation). Relativistic effects are also neglected as they contribute little to valence properties. Although theoretical work (*9, 10*) directed at understanding the limitations of these two approximations has been reported, this is outside the scope of this article. With these approximations the Hamiltonian operator (in atomic units) can be written as

$$\hat{H} = -\frac{1}{2}\sum_{i=1}^{n}\nabla_i^2 - \sum_{A=1}^{N}\sum_{i=1}^{n} Z_A r_{Ai}^{-1} + \sum_{i>j=1}^{n} r_{ij}^{-1} + \sum_{A>B=1}^{N} Z_A Z_B R_{AB}^{-1} \tag{2}$$

where Z is the nuclear charge, r_{ij} is the electron-electron distance, r_{Ai}

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is the electron-nuclei distance, and R is the internuclear distance. The four terms in Eq. 2 account for the electron kinetic energy, the nuclear-electron attraction, the electron repulsion, and the nuclear repulsion contributions, respectively. The summations extend over n electrons and N nuclei in the system. The difference with classical mechanics is apparent in the electron kinetic energy, where $1/2\ mv^2$ has been converted to a differential operator as a result of the small electron mass.

The solution of the Schrödinger equation is very challenging, even with the Hamiltonian operator in Eq. 2. Methods such as Monte Carlo (*11*) are difficult to apply, because of the high precision required. For example, the dissociation energy (D_e) of N_2 (228 kcal/mol) is a small fraction of the total electronic energy of more than 65,000 kcal/mol. Most quantum mechanical methods rely on a two-step procedure. In the first step, the molecular orbitals (MOs) are obtained as a linear combination of one-particle basis functions

$$\psi_i = \sum_{\mu} \chi_{\mu} C_{\mu i} \tag{3}$$

where the χ_{μ}s are commonly referred to as AOs. These AOs include functions to describe the atoms as well as higher angular momentum functions called a polarization functions to describe the distortion that occurs as a result of bonding in molecules. The simplest approach to obtaining the MO coefficients $\mathbf{C}$ is the self-consistent-field (SCF) approximation, where each electron is assumed to move in the average field of all others. The occupied MOs are consistent with chemical intuition: the core orbitals are very atomic-like, and the valence orbitals can be classified as bonding orbitals or lone pairs.

Although insight into the bonding can often be achieved at the SCF level, to achieve accurate energetics it is generally necessary to account for the instantaneous interaction between the electrons in a second step. The energy lowering relative to the SCF has been termed the electron correlation energy. Most solutions to the electron correlation problem also use an expansion technique, where the basis functions are antisymmetrized (due to the fact that electrons are fermions) n-fold products of MOs. These n-particle functions are often termed configuration state functions (CSFs). The correlation (or n-particle) problem can be solved exactly for a given MO basis if all possible CSFs are included in the expansion—an FCI calculation. However, because the n-particle basis set in the FCI procedure has a factorial dependence on the number of electrons and MOs, it rapidly becomes computationally intractable. Three approximate methods of treating the correlation problem are in common use: Møller-Plesset (MP) perturbation theory (*12*), coupled cluster (CC) approaches, and CI approaches. [See (*13*) for a more complete description of computational methods.] All of these methods rely on truncating the CSF expansion. This is generally done by restricting the number of MO replacements (that is, single, double, triple, . . . replacements or excitations) relative to either the SCF reference or a suitable multireference wave function.

Because most quantum mechanical solutions involve a double basis set expansion, the differences between calculated and accurate experimental quantities may arise from limitations in either expansion. This fact underlies the importance of the FCI method, as for a given AO basis it represents the exact solution of the correlation problem and therefore provides an unambiguous standard with which to compare approximate treatments of correlation. Although this fact has been realized for some time, it is only recently that FCI calculations in which realistic one-particle basis sets are used have become possible. The development of highly efficient algorithms (*6, 7*) for solving the FCI problem combined with computer architectures such as the CRAY 2, with its very large central memory and its ability to perform matrix multiplication at nearly 300 MFLOPS, increased the size of the FCI problem that could be treated by more than an order of magnitude. This permitted a series of benchmark calculations (*2*) not only for total energies but for a wide variety of molecular properties. An important conclusion from the benchmark studies was that a complete-active-space SCF (CASSCF) calculation followed by an MRCI treatment accurately reproduced the FCI results. The CASSCF method can be considered an extension of the SCF method, where the most important correlation effects are included in the MO optimization step. This approach defines a reference wave function comprising the most important CSFs for the MRCI procedure. In addition, the SCF-based CCSD(T) method and the analogous quadratic CI [QCISD(T)] method (*14*) have been shown to give good agreement with the FCI, except for cases (*15*) where the system is very multireference in character, such as stretched bonds or transition-metal multiple bonds or in regions of curve crossings. Thus, the FCI benchmark calculations indicated that most of the discrepancy with experiment in many of the earlier calculations was due to the truncation of the one-particle basis set rather than the n-particle expansion.

The realization that a significant fraction of the remaining error in high-quality ab initio calculations was due to the incompleteness of the one-particle basis resulted in an impetus (*16, 17*) to develop improved basis sets. The one-particle basis functions (or AOs) are commonly composed of a linear combination of individual Gaussian functions called primitives. The accuracy of the one-particle basis set depends not only on the number and choice of primitives but also on the contraction coefficients that define the transformation from primitives to AOs. The older basis sets were developed at the SCF level, whereas the new one-particle sets are designed explicitly for correlated calculations. One class of these has been termed atomic natural orbital (ANO) basis sets (*16*), as the contraction coefficients are determined from single and double configuration-interaction (SDCI) calculations on atoms (or based on averaged sets for neutral atoms and negative ions) using large primitive sets. Because the occupation numbers of the natural orbitals of the SDCI are the criterion for including the contraction in the basis set, these sets could be systematically expanded to approach the one-particle limit. Thus, it is possible to approach the complete CI result (the exact result in the nonrelativistic limit and Born-Oppenheimer approximation) by carrying out an MRCI calculation to account for electron correlation in a nearly complete one-particle basis. On the basis of comparison with FCI calculations in a smaller but realistic basis, the MRCI calculation is expected to account for all important valence correlation effects. The assumption of a small coupling between the one- and n-particle expansions is generally good for properties that depend on the energy but may be suspect for properties such as hyperfine coupling constants (*2*).

As an example of FCI benchmark studies, we present in Table 1 the results of a study (*18, 19*) of the energy separation between the $^1A_1$ and $^3B_1$ states in methylene. In the upper portion of the table we compare the separations computed by using approximate correlation methods with the FCI result in a double-zeta plus polarization (DZP) quality basis set. The error is very large at the SCF level because the $^3B_1$ state is much better described by one reference configuration than is the $^1A_1$ state. Although the error is significantly less at the SDCI level, the separation is still not within chemical accuracy ($\approx$1 kcal/mol). If an estimate for higher than double excitations is made by using either the Davidson's correction (Q) (*20*) or the coupled pair functional (CPF) method (*21*), the error is reduced to less than 1 kcal/mol. However, the CASSCF/MRCI treatment is in nearly exact agreement with the FCI. Thus, a CASSCF/MRCI calculation, in which a nearly complete one-particle basis set is used, should produce a separation in excellent agreement with the accurate experimental value (*22*).

In the lower portion of Table 1 we show the effect of systemati-

Table 1. Theoretical study of $^1A_1$–$^3B_1$ separation in CH_2 (kcal/mol). The error is the difference from the FCI value.

Method	Separation	Error
Calibration of n-*particle treatment in a small basis set*		
SCF	26.14	14.17
SCF/SDCI	14.63	2.66
SCF/SDCI+Q	12.35	0.38
CPF	12.42	0.45
CASSCF/MRCI	11.97	0.00
FCI	11.97	
Calibration of one-particle treatment at MRCI level		
[3*s* 2*p* 1*d*/2*s* 1*p*]	11.33	
[4*s* 3*p* 2*d* 1*f*/3*s* 2*p* 1*d*]	9.66	
[5*s* 4*p* 3*d* 2*f* 1*g*/4*s* 3*p* 2*d*]	9.24	
Experiment + theory (T_e)	9.28 (±0.1)	

cally expanding the one-particle basis set. (The notation indicates the number and type of contracted ANO functions on C and H, respectively.) Because the separation decreases with improvement in the one-particle basis set, several sets of polarization functions are required to achieve very accurate results. The valence limit is estimated to be about 9.1 kcal/mol, on the basis of the convergence of the separation with basis set. This value is slightly less than the energy separation neglecting zero-point motion (T_e) deduced (*22*) from the experimental adiabatic value (T_0) and the experimental and theoretical zero-point corrections. This discrepancy is due mostly to the effects of inner-shell (C 1*s*) correlation, which has been estimated (*19*) to increase the separation by 0.35 kcal/mol.

Unlike the CH_2 example described above, it is not always possible to investigate the convergence of the one-particle basis set with the use of a correlation treatment that accurately reproduces the FCI result. Thus, it may be necessary to add the effect of expanding the one-particle basis (at a moderate level of correlation treatment) to the result obtained at a high level of correlation treatment in a modest-sized basis set. Again we stress that this is often a good approximation for total energies, but not necessarily so for molecular properties. A notable example of this approach is the G2 theory of Pople and co-workers (*23*). [The G2 approach is an improved version of the G1 method (*24*).] In the G2 approach the QCISD(T) method is used to solve the *n*-particle problem accurately, and MP methods are used to determine the one-particle basis set correction. Large basis set calculations are possible because the MP2 method has been implemented with an approach that requires little disk space.

New Problems Solved by Calculations

C–H bond energies. The value for the C–H bond dissociation energy in acetylene, D_0(HCCH–H), is controversial, primarily because of several disparate experimental values (*25–29*). Before 1989, kinetics experiments (*25*) gave a value between 124 and 127 kcal/mol, while the photodissociation and photoionization experiments of Lee and co-workers (*26*) gave a value of about 132 kcal/mol. In 1989, the photodissociation experiments of Segall *et al.* (*27*) were interpreted in terms of a bond energy of 127 ± 1.5 kcal/mol, and the Stark anticrossing spectroscopy experiment of Green *et al.* (*28*) was interpreted as showing an upper bound of 126.647 kcal/mol. However, these values were inconsistent with another highly accurate measurement of 131.3 ± 0.7 kcal/mol by Ervin *et al.* (*29*), who used the techniques of negative-ion photoelectron spectroscopy and gas-phase proton transfer kinetics.

Because current theoretical methods are capable of computing C–H bond dissociation energies to an accuracy of about 1 kcal/mol, attempts were made to resolve this controversy theoretically (*30–33*). Curtiss and Pople (*30*) calculated the bond energy using the G1 approach. Their value of 133.5 ± 2.3 kcal/mol favored the higher experimental values, but the uncertainties (due to limitations in the empirical corrections inherent in the G1 method) precluded a definitive resolution. More recently, several additional theoretical studies have been performed. Calculations by Bauschlicher *et al.* (*31*), using the CPF and CASSCF/MRCI approaches and extensive one-particle basis sets, gave a D_0 value of 130.1 ± 1.0 kcal/mol, where the error bars represent 90% confidence limits. The theoretical calculations of Montgomery and Petersson (*32*) used the QCISD(T) method. As in the two other theoretical studies, they were able to estimate the remaining errors in the one-particle basis set. Their value of 131.54 kcal/mol (with an estimated error of 0.51 kcal/mol based on the root-mean-square error in the bond energies of other molecules) is in excellent agreement with the theoretical value of Bauschlicher *et al.* (*31*).

Because the heats of formation of C_2H_2 and C_2 are well known, the C–H bond dissociation energy of acetylene can be deduced from an accurate C–H dissociation energy of C_2H. We determined (*34*) the C–H energy in C_2H to be 112.4 ± 2.0 kcal/mol, in excellent agreement with the very recent experimental value (*35*) of 112.0 ± 0.8 kcal/mol. The sum of our C–H bond energies for C_2H_2 and C_2H is in excellent agreement with the difference in the heats of formation of C_2 and C_2H_2. Thus the theoretical calculations rule out the lower experimental determinations of the C–H bond dissociation energy of acetylene. This work is presently being extended to the C–H bond energies of other hydrocarbons in order to improve the thermodynamic basis of combustion models.

Vibrational frequencies of O_3. Another area where quantum mechanical calculations have made great progress in the past few years has been in the calculation of vibrational frequencies of polyatomic molecules (*36*). Because the changes in the molecule with a bond stretch or bend are much smaller than for bond breaking, quantitative results are often obtained even at the SCF level. This is significant as efficient codes are available to determine analytically the first, second, and third derivatives of the energy with respect to nuclear motion (*37*). However, to obtain good agreement with the experimental frequencies, it is necessary to account for both correlation and anharmonicity effects. We illustrate the current state of the art in this area by reviewing work on the O_3 molecule (*38*), which is challenging theoretically because of the biradical character of the $^1A_1$ ground state.

The vibrational levels of O_3 are poorly described at low levels of theory, resulting in an incorrect ordering of the symmetric and antisymmetric stretching frequencies in many cases. Although the CASSCF method provides the correct ordering and reasonably good frequencies, the subsequent MRCI calculation is prohibitively expensive in a high-quality one-particle basis set. However, the single reference–based CCSD(T) method gives remarkably good agreement with experiment (*39*). The CCSD(T) geometry agrees with experiment to within 0.001 Å and 0.3°. The computed fundamental vibrational frequencies ν are in error by only 2 cm^{-1} for the symmetric stretch and bend. Even the antisymmetric stretch, which has eluded quantitative theoretical treatment, is in error by only 67 cm^{-1}. The theoretical (experimental) values are: $\nu_1(a_1)$ = 1105(1103), $\nu_2(a_1)$ = 699(701), and $\nu_3(b_2)$ = 975(1042) cm^{-1}. Because the CCSD approach without the perturbational estimate of the triple excitations has errors that are 200 cm^{-1} larger, the triples estimate must be included for accurate results. Because CCSD(T) analytic derivatives are available (40), we expect this method to have great utility for many other molecular systems.

The Lewis-Rayleigh afterglow and the Hermann infrared system of N_2. The Lewis-Rayleigh afterglow of N_2 is known to occur through a three-body recombination of ground-state N atoms followed by collisional energy transfer. Because most of the emission originates from the first positive bands ($B^3\Pi_g - A^3\Sigma_u^+$ and the $B^3\Pi_g$ state does not dissociate to ground-state atoms, a precursor state must be involved. In the 1950s two theories were proposed with respect to the identity of the precursor state. The $A'^5\Sigma_g^+$ state was proposed to be the precursor of the Lewis-Rayleigh afterglow in the theory of Berkowitz, Chupka, and Kistiakowsky (*41*). This theory was criticized by Campbell and Thrust (*42*) on the basis that the $A'^5\Sigma_g^+$ state was too shallow to support an appreciable steady-state population based on the then-accepted value (*43*) of 850 cm^{-1} for the well depth. They invoked instead the $A^3\Sigma_u^+$ state as the precursor. However, on the basis of MRCI calculations in an extended one-particle basis set, we computed (*44*) a $A'^5\Sigma_g^+$ potential with a well depth of 3450 cm^{-1}, a barrier to dissociation of about 500 cm^{-1}, and a van der Waals minimum of about 47 cm^{-1}. The larger well depth removes the objection to $A'^5\Sigma_g^+$ as the precursor state for the afterglow.

Kumar and Kumar (*45*) have studied the relative vibrational intensities of the first positive system in the afterglow spectra of N_2 in the range from 1900 to 8000 Å at 77 and 300 K. As the temperature is lowered from 300 to 77 K, the overall intensity of the bands increases and there is a shift in the relative intensities with the maximum emission occurring from the $v' = 12$ instead of the $v' = 11$ level of the $B^3\Pi_g$ state. As the temperature is further decreased to that of liquid helium, the afterglow occurs primarily from only the $v' = 6$ level (*46*). Figure 1 shows the $B^3\Pi_g$, $A^3\Sigma_u^+$, and $A'^5\Sigma_g^+$ potential curves and their vibrational levels in the region of interest. The states are colored to facilitate distinguishing the vibrational energy levels. We were able to use these potentials to explain the variation in the emission from the $B^3\Pi_g$ state as a function of temperature. At 300 K the maximum intensity originates from the $v' = 11$ level, because the $A'^5\Sigma_g^+$ state is vibrationally relaxed before intersystem crossing to the $B^3\Pi_g$ state, and the lowest vibrational level of the $A'^5\Sigma_g^+$ state most efficiently crosses to the $v' = 11$ level of the $B^3\Pi_g$ state. At 77 K, an outer van der Waals well in the A' state (not shown in Fig. 1) allows for tunneling to the higher vibrational levels of the inner well of the $A'^5\Sigma_g^+$ state. Because there are fewer collisions at this temperature, intersystem crossing to the $v' = 12$ level of the $B^3\Pi_g$ state is more rapid than collisional relaxation, causing the maximum intensity in the $B^3\Pi_g$ state emission to increase from $v' = 11$ to $v' = 12$. At 4 K the barrier in the A' state leads to a cutoff in the emission from $v' = 10$ to 12. However, the $A'^5\Sigma_u^+$ state has no barrier and therefore it can populate the $B^3\Pi_g$ state even at 4 K. The $A'^5\Sigma_u^+$ and $B^3\Pi_g$ potential curves cross at $v = 16$ in the $A'^5\Sigma_u^+$ state and $v' = 6$ in the $B^3\Pi_g$ state, thereby giving a maximum in emission for the $v' = 6$ level of the $B^3\Pi_g$ state at 4 K. The barrier in the $A'^5\Sigma_g^+$ state yields a quasi-bound level that allows intersystem crossing to $v' = 13$ of the $B^3\Pi_g$ state, thus explaining why this level has the same population mechanism as $v' = 12$, even though $v' = 13$ is above the dissociation limit.

The Hermann infrared system (HIR) of N2 observed (*47*) in the region from 700 to 970 nm had eluded assignment for nearly 40 years. Carroll and Sayers (*48*) were able to determine that the HIR bands result from either a triplet or quintet transition. Furthermore, from the work of Nadler *et al.* (*49*) it was known that the HIR system is readily generated by the energy pooling reaction between metastable $N_2(A'^5\Sigma_u^+)$ molecules, which demands that the upper state be less than 12.02 eV above the ground state. In addition, positions of four vibrational levels of the upper and five of the lower state were known. This later fact precluded assigning $A'^5\Sigma_g^+$ as the lower state of the transition, because it was inconsistent with a well depth of only 850 cm^{-1}. However, our recent theoretical $A'^5\Sigma_g^+$ state potential produced vibrational spacings in excellent agreement with the observed ones. Given this fact, it was straightforward to assign (*44*) the HIR band system to the $C''^5\Pi_g \rightarrow A'^5\Sigma_g^+$ transition. Recently this assignment has been confirmed spectroscopically by Huber and Vervloet (*50*).

This example demonstrates that theory is capable of assigning and predicting new band systems. Theoretical calculations for band strengths and radiative lifetimes are also approaching quantitative accuracy. For example, calculations (*51*) for the radiative lifetime of the OH ultraviolet system are accurate to 5%, which is sufficient to discriminate between conflicting experimental determinations. Further examples of the utility of theory for predicting spectra of both diatomic and polyatomic molecules can be found in a recent review article (*52*).

Identification of the ground state of Al_2 *and* Si_2. Until recently the ground state of Al_2 was not known. The three states, ${}^3\Sigma_g^-$, ${}^3\Pi_u$, and ${}^1\Sigma_g^+$, that dissociate to the ${}^2P(3s^23p^1)$ ground state of Al atom were all proposed as candidates. Although qualitative theoretical calculations (*53*) were able to exclude the ${}^1\Sigma_g^+$ state, the two triplet states were too close in energy to definitively assign the ground state. However, we used extensive MRCI calculations (*54*) calibrated against FCI benchmarks and extensive one-particle basis set calibrations to predict a ${}^3\Pi_u$ ground state, despite a $A^3\Sigma_g^- - X^3\Pi_u$ separation of only 174 cm^{-1}. This is remarkable considering that 10 years ago a computed separation of 1000 cm^{-1} would not have been considered definitive. Recent experiments (*55, 56*) have confirmed that Al_2 has a ${}^3\Pi_u$ ground state, but the $A^3\Sigma_g^-$ excitation energy has not yet been measured.

Another important molecule for which the ground state was not known until recently is Si_2. Although valence isoelectronic with C_2, which has a ${}^1\Sigma_g^+$ ground state, the much weaker multiple bonding in Si_2 precludes a ${}^1\Sigma_g^+$ ground state. Instead, by analogy with Al_2, the

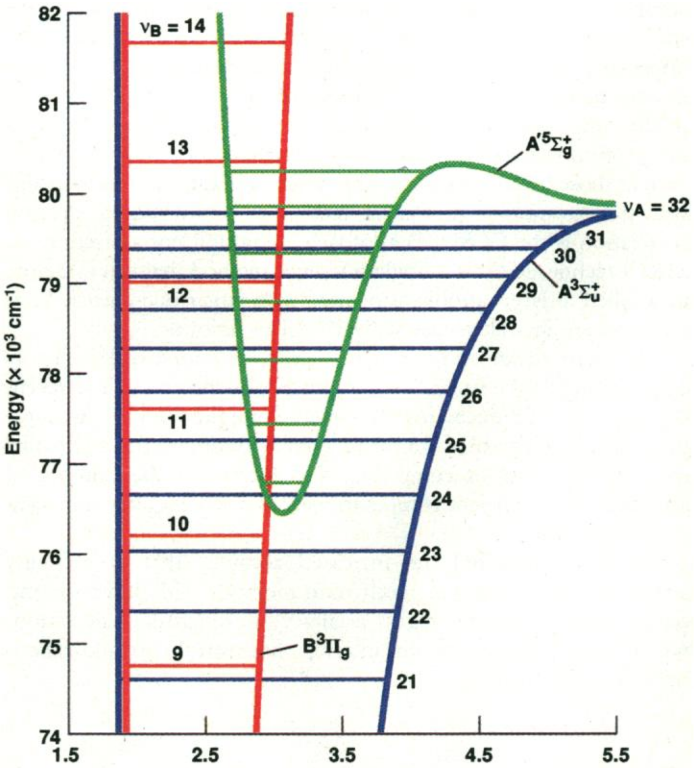

Fig. 1. Potential energy curves and vibrational levels for the $A^3\Sigma_u^+$, $A'^5\Sigma_g^+$, and $B^3\Pi_g$ states of N_2 drawn in blue, green, and red, respectively. The vibrational levels of the $B^3\Pi_g$ state are calculated using the Wentzel-Kramers-Brillouin formalism and the $A'^5\Sigma_g^+$ levels are the quantum mechanical values from table VII of (*44*).

two lowest electronic states are $^3\Pi_u$ and $^3\Sigma_g^-$. The $^3\Sigma_g^-$–$^3\Pi_u$ separation is sensitive to the level of treatment, so that extensive theoretical calculations are required for definitive results. Lüthi and McLean (*57*), using an extended basis set and accounting for electron correlation at the MRCI level, found that the $^3\Sigma_g^-$ state lies 522 cm^{-1} below $^3\Pi_u$. They then corrected this number on the basis of analogous calculations for C_2 where the separation is well known. This led to a triplet separation of 180 ± 200 cm^{-1} for Si_2 with the $^3\Sigma_g^-$ state lower. However, the use of C_2 as a calibrant is questionable. The different bonding in C_2 and Si_2 is reflected by the fact that the $^3\Sigma_g^-$ state of C_2 lies 5718 cm^{-1} above the $^3\Pi_u$ state.

In our investigation (*58*) of the triplet separation in Si_2, we carried out a systematic study of the effect of improving the one-particle basis set and used FCI benchmark calculations to calibrate our MRCI treatment of electron correlation. Our best estimate for the $A^3\Pi_u$–$X^3\Sigma_g^-$ separation was **440 ± 100 cm^{-1}**, with a value more likely in the upper half of the range. Recently, Neumark and co-workers (*59*) determined a value of 669 ± 80 cm^{-1} for the triplet separation on the basis of photodetachment experiments on Si_2^-. These values are in reasonable agreement considering that our upper bound and their lower bound differ by only 50 cm^{-1}. This again illustrates that very accurate energy separations can be computed if performed in conjunction with calibration calculations for the completeness of both the one- and *n*-particle expansions.

Concluding Remarks

In this review we have stressed that by combining basis set saturation studies, which assess the convergence of the one-particle basis, and FCI calculations, which assess the completeness of the *n*-particle expansion, molecular wave functions of unprecedented accuracy can be obtained. Theoretical benchmark calculations have shown that the CASSCF/MRCI approach accounts for all of the important valence correlation effects and have also shown that shortcomings of earlier calculations were often a result of limitations in the one-particle, as opposed to the *n*-particle, expansion. This observation was the impetus for the development of new basis sets, such as those based on ANOs. The benchmark calculations have also shown that another promising technique for including electron correlation is the CCSD(T) approach. Although not as accurate as MRCI techniques, it is a single-reference method that can therefore be applied to larger problems or used with larger one-particle basis sets than are feasible to use with MRCI techniques.

The rapid advance in computer hardware is one of the factors contributing to the success of computational chemistry. The recent development of reduced instruction set computer (RISC) architecture, such as in the IBM RS/6000, is contributing to this success by reducing the cost of computing and increasing the number of scientists with sufficient computational resources to carry out accurate calculations.

We have illustrated the increased accuracy that is presently achievable with quantum mechanical methods with several examples. We expect that the higher accuracy of present-day calculations will allow for an even greater interplay between theory and experiment in the future.

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