Towards Numerical Solutions of the Schrödinger Equation for Diatomic Molecules

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Many-body perturbation and coupled-cluster methods using numerical Hartree-Fock and correlating orbitals are applied to diatomic molecules for the first time. For LiH, the correlation energy is within 0.001 a.u. of the nonrelativistic correlation energy limit, which provides an energy of -8.069 a.u. compared to the exact result of -8.070. These results suggest that highly accurate results for diatomic molecules may be obtained by the proposed approach.

Following the development of many-body perturbation theory (MBPT) by Brueckner and Goldstone,[1,2] Kelly made the initial applications to correlation energies and other properties of atoms.[3-5] By exploiting the spherical atomic symmetry, which permits separation of the radial equation from the angular part, these calculations were performed purely numerically. These applications included the second and third orders of perturbation theory with some consideration of higher-order diagrams via denominator shifts. Kelly and co-workers[6,7] attempted to use one-center-expansion techniques for some molecules (H_2, HF, H_2O) to retain the same numerical approach as for atoms, but this was generally unsatisfactory due to the extreme difficulty in correctly describing the effect of the Coulomb potentials associated with the different nuclear centers in molecules.

To rectify the multicenter problem, MBPT could be performed using the conventional Slater- or Gaussian-type basis sets employed in molecular theory. This basis-set MBPT approach was accomplished and presented in a series of papers by Bartlett and co-workers[8-10] which has since led to extensive numbers of MBPT applications[11] [also referred to in some circles as MP (Moller-Plesset) perturbation theory[12]]. In general these applications explicitly include contributions from diagrams of higher-order than Kelly considered—typically all diagrams through fourth-order perturbation theory.[11] Futhermore, infinite-order coupled-cluster (CC)[13,14] generalizations of MBPT have now been implemented; these are CC methods which include T_2 cluster operators (CCD), all diagrams resulting from T_1 and T_2 cluster operators (CCSD)[10,15] and their products, and partial contributions of T_3 (CCSDT-1).[16] However, even though these methods treat much higher categories of correlation diagrams than in most MBPT applications, they retain an error due to basis-set limitations that was virtually eliminated in Kelly's initial atomic calculations. This follows since the asymptotic dependence of corre-

lated calculations such as CCSD, e.g., scales as n^6 for n-basis functions, and CCSDT-1 as n^7. This places a severe restriction on the number of basis functions that may be employed in molecular calculations, and, consequently, it is seldom possible to extrapolate to the basis-set limit for molecules.

Because of the separation of the angular and radial parts in confocal, elliptical coordinates, diatomic molecules are one molecular category that allows purely numerical solutions in analogy with those for atoms.[17,18] Hence, it is of much interest to combine numerical solutions for diatomic molecules with the infinite-order summations of diagrams afforded by coupled-cluster theory to attempt to approach the basis-set-limit solution of the Schrödinger equation. When future methods permit purely numerical results for polyatomic molecules to be achieved, a similar strategy for using numerical basis sets as presented below for diatomic molecules should be generally applicable to introduce electron correlation to a Hartree-Fock (HF) starting point. The alternative of actually solving the CC equations numerically, instead of just using a numerical basis set, has been accomplished for atoms[19] and an analogous approach would be highly desirable for diatomic molecules, but the same strategy for atoms would be computationally prohibitive for molecules. In this initial attempt we will limit ourselves to a numerical basis set.

Methods for obtaining numerical self-consistent-field (SCF) and multiconfiguration–self-consistent-field (MCSCF) solutions for diatomic molecules have been developed by McCullough and Adamowicz.[17,18] This technique provides occupied HF orbitals, while a treatment of the correlation problem also requires a mechanism to generate an appropriate set of correlating orbitals.

To define excited correlating orbitals, we employ the idea of the Bethe-Goldstone (BG) hierarchy of equations used for the first time by Nesbet[20] to correlate electrons. In this scheme, the many-electron problem

is partitioned into two-, three-, etc., electron fragments, and then electrons of only one fragment at a time are allowed to correlate while the rest remain in their HF states. For example, for two-electron fragments this can be accomplished by a variational calculation with a configuration-interaction- (CI-) type wave function in which only determinants with single and double excitations from the particular two occupied orbitals are included:

$$\psi_{ij} = \psi_0 + \sum_a c_i^a \psi_i^a + \sum_b c_j^b \psi_j^b + \sum_{ab} c_{ij}^{ab} \psi_{ij}^{ab}. \quad (1)$$

Similarly, ψ_{ijk} is used for three-electron fragments, ψ_{ijkl} for four, etc. For two-electron fragments, BG equations become identical with independent-electron-pair (IEPA) equations.[21,22]

For our present purpose we use the concept of the BG fragmentation with independent variational, correlated numerical (MCSCF) calculations for each two-electron fragment. The union of the correlating numerical MCSCF orbitals generated in this procedure constitute the excited-orbital basis set, while the occupied orbitals are represented by their HF solutions.

Stepwise, following a partitioning into two-electron fragments and independent MCSCF calculations, we assemble a common orbital set and evaluate the one- and two-electron integrals. Using the common basis set, an SCF calculation is performed which keeps occupied orbitals unchanged but combines the correlation orbitals into a set of functions which diagonalize the Fock operator. At this point linearly dependent orbitals are removed.[23] These solutions to the matrix Fock equations are then used in the CC calculations to facilitate immediate MBPT comparisons with HF-based basis-set approximations, rather than just orthogonalizing the excited orbitals among themselves. Of course in CC theory, the results would be independent of such a transformation among the excited orbitals.[11]

Calculations have been performed for the H_2 and LiH molecules and the results are reported in Table I. Forty-five MCSCF numerical orbitals of σ, π, and δ symmetry were obtained for the H_2 molecule. Of course, since the BG pair equation for this case is exactly equivalent to the Schrödinger equation, the coveraged CCSD energy should be exactly the variational MCSCF result in the same basis set, as indicated. The current CCD, CCSD, and MCSCF results should be nearly saturated in the $\sigma\pi\delta$ space, while further improvements could be introduced by additional ϕ orbitals.

An apt comparison is offered by the very accurate MBPT-CC results of Jeziorski et al.[24] With use of large, explicitly correlated Gaussian geminal (GG) basis sets which expand each pair in forty such functions that are then extensively optimized by minimizing the second-order Hylleraas functional, practically saturated values for the second- and third-order corre-

lation corrections and CCD have been obtained. The current numerical-basis-set results are in excellent agreement, although they differ in finite orders primarily because of incompleteness in neglecting ϕ and higher functions. The infinite-order CCD is in much better agreement apparently due to some cancellations in finite orders. The inclusion of single excitations via CCSD accounts for -0.00013 a.u.

For the LiH molecule calculations have been performed using seventy numerical MCSCF orbitals, also of σ, π, and δ symmetry. These orbitals were generated by independent MCSCF calculations for the $(1\sigma)^2$, $(2\sigma)^2$, $(1\sigma 2\sigma)$ singlet and triplet coupled electron pairs. In this basis set our CCD energy is already slightly closer to the experimental value than the GG result, again showing cancellation in lower orders of perturbation theory. Adding in single and triple excitations with our CCSDT-1 model[16] we obtain -0.08183 a.u., in comparison to the nonrelativistic limit of -0.083 a.u.[26] This is a highly accurate result to the Schrödinger equation for a molecule with more than two electrons.

Another pertinent comparison is with the multireference single and double CI (MRSDCI) 168-contracted Gaussian-function (i.e. 111 counting π, δ, ϕ, γ as single functions) results of Handy et al.[26] This result of -0.08169 a.u. is a rigorous upper-bound to the exact correlation energy, and is in excellent agreement with our values. Unlike CI, the CC methods are not rigorously variational, although they may be shown to be upper bounds up to some order in perturbation theory, and, except for pathological cases, in practice show upper bound character in comparison to full CI[27] (i.e., the best possible basis-set result).

In conclusion, the expansions of CC correlation functions in terms of one-electron-orbital products are capable of giving very accurate results (about 99% of the correlation energy for the H_2 and LiH molecules) even within a limited range of the angular momenta (in the present calculations through δ only) provided that correlation orbitals are well optimized. Secondly, the answers are as good as those using two-electron geminal basis functions, but unlike the latter, which are currently limited to s-type geminals, this technique can be applied to much more complicated diatomic molecules. Thirdly, using seventy numerical orbitals and CCSDT-1 our results are comparable to the effective basis-set-limit LiH result, which employs 111 contracted Gaussian orbitals. Fourthly, the BG method of variationally correlated fragments (pairs) offers a promising procedure for spanning the correlating orbital space for very accurate CC calculations.

The procedure proposed can be applied to any diatomic molecule. In particular, the very interesting and controversial results for transition-metal diatomics like Cu_2[28] and Cr_2[29] suffer from the basis-set limitations.

TABLE I. Comparison of MBPT [$E(2)$, $E(3)$, and $E(4)$] and coupled cluster (CCD, CCSD, and CCSDT-1) correlation energies for H_2 and LiH molecules obtained by using explicitly correlated Gaussian geminals, Slater and Gaussian orbitals (for LiH), and numerical orbitals. All quantities are in atomic units.

	40 GG[a]	H_2 45 numerical orb. $(18\sigma,15\pi,12\delta)$
$E(2)$	−0.03421	−0.03334
$E(3)$	−0.00438	−0.00507
$E(4)$	−0.00143[b]	−0.00148
CCD	−0.04041	−0.04037
CCSD		−0.04051
MCSCF		−0.04051[c]
Experiment[a]		−0.0408

	160 GG[d]	LiH 32 Slaters[e] $(18\sigma,10\pi,4\delta)$	70 numerical orb. $(30\sigma,24\pi,16\delta)$	111 Gaussian Orb.[h] $(54\sigma,33\pi,17\delta,6\phi,1\gamma)$
$E(2)$	−0.07217	−0.06539	−0.07025	
$E(3)$	−0.00689	−0.00983	−0.00866	
$E(4)$	−0.00193[b]	−0.00225	−0.00210[f]	
CCD	−0.08148[g]	−0.07798	−0.08152	
CCSD		−0.07816	−0.08167	
CCSDT-1		−0.07829	−0.08183[f]	
MRSDCI				−0.08169[h]
Experiment[a]			−0.0832 ± 0.0001	

[a]Gaussian geminal and experimental results for H_2 and LiH have been taken from Ref. 24.

[b]Double and quadruple excitation diagram contributions only.

[c]Full MCSCF optimization of all 45 diagonal configurations.

[d]Each electron pair function has been expanded in its own basis set of 40 GG's.

[e]Slater basis set, $E(2)$ and $E(3)$ are from Ref. 5. This is a typical normal basis calculation.

[f]The fourth-order triple excitation contribution was calculated with use of a truncated basis set of 58 numerical orbitals.

[g]Currently the authors of Ref. 24, after revision of their strong orthogonality parameters, recommend a new slightly lower value of 0.08151 a.u.

[h]This is the largest basis-set result for LiH reported (Ref. 26). The energy was evaluated by a MRSDCI consisting of 132015 C_{2v} symmetry adapted configurations.

The current approach should contribute to diminishing the effect of this restriction in the *ab initio* results.

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