Chapter 7
Exoduction
This thesis is mostly concerned with MRMP, and some consideration is given to MRCI and MRCEPA(0). Looking back upon the previous chapters it is learnt that an efficient and size consistent multi-reference perturbation method for calculating correlation energies can be constructed. To achieve size consistency the form of the zeroth-order Hamiltonian has to be constructed from projection operators that project onto subspaces of a single excitation level only. In practice it is possible to define a whole family of zeroth-order Hamiltonians that meet this requirement. In particular a zeroth-order Hamiltonian with as few as possible off-diagonal terms may be chosen. Besides choosing a proper zeroth-order Hamiltonian the choice for the orthogonalisation method to construct the excited state space is essential. Perturbation theory proves to be rather sensitive to numerical errors in the orthogonalisation. Because the errors are different for calculations of different size they can lead to considerable size consistency errors.

Despite the fact that a size consistent multi-reference approach to correlation energy calculations has been obtained the correlation problem is not solved yet. It should be realised that perturbation theory is not stable enough to be used in all cases; On the other hand MRCI corrected for size consistency errors and MRCEPA(0) are only approximately size consistent. However they may be applicable in cases where perturbation theory fails.

Although not too much thought was given to the size consistency corrected MRCI (MRCI+Q) and the MRCEPA(0), the MRMP chapters allow for a comparison. For closed shell cases MRCI+Q and MRCEPA(0) yield small size consistency errors. However, in the open-shell cases the behaviour was rather poor. In every case MRCEPA(0) performed better with respect to size consistency than MRCI+Q. Regarding the stability of these methods it should be noted that the MRCI approaches as well as MRCEPA(0) converged in all calculations. This meant that MRCEPA(0) at the moment is the best alternative to MRMP we have available, and this method should be considered in cases where MRMP is hampered by divergences.

Reconsidering these results we may relate them to the list of requirements that was compiled in the introduction to this thesis.
1) A problematic point with perturbation theory is that it is not well defined for all chemically reasonable geometries. This problem was long known for single-reference perturbation theory. One might have hoped that this problem could be solved using a multi-reference approach since one expects that the perturbation would be smaller in such a treatment. However, the contrary may be the case. In calculations on O$_2$ the multi-reference approach yielded a larger difference between $E_0$ and $E_1$ than the single-reference treatment. So the perturbation is larger in the multi-reference case. Indeed, the multi-reference calculations are more strongly divergent than the single-reference ones. Although a method is suggested to detect divergences so that these points may be avoided in calculating potential energy surfaces, a MRMP study may be impossible if too many divergent points are present. MRCI is not subject to divergence problems. MRCEPA(0) shows to be well behaved in the calculations documented in this thesis. However, it is to be expected that MRCEPA(0) may diverge if an inadequate reference space is used.

2) MRMP, MRCI, and MRCEPA(0) are able to dissociate molecules properly if the reference wavefunction is chosen judiciously.

3) MRMP, MRCI, and MRCEPA(0) are invariant for orbital rotations that leave the reference wavefunction unchanged.

4) MRMP may be implemented in a such way that exactly size consistent results may be obtained. This is an important result because there was a growing tendency to believe that multi-reference approaches could not be size consistent except for some special cases. MRCI and MRCEPA(0) fail with respect to this requirement especially in open shell cases.
5) The MRMP approaches sometimes have problems in calculating energies of a similar quality at a wide range of geometries. For example MRMP2 may not be accurate enough in calculating dissociation energies. In most cases this could be mended in the next order of perturbation theory. However, one case was found in which the MRMP3 gave less accurate results than MRMP2 (see chapter 2, table V). With respect to dissociation energies MRCI and MRCEPA(0) behave very well.

6) Considering efficiency MRMP is at least an order of magnitude more efficient than MRCI or MRCEPA(0). MRMP3 costs about as much as a single CI-iteration. This means that for large molecules MRMP may be the only reasonable approach to take correlation energy into account. This was one of the strong motivations for Andersson et al. [1] to develop CASMP2.

Concluding, we have found that MRMP satisfies the requirements we listed except that it may diverge and the quality of the energy may be insufficient. The most appropriate alternative currently available, MRCEPA(0) fails in obtaining size consistency in open shell cases and it is relatively expensive. A reasonable scheme for calculating potential energy surfaces therefore seems to first try MRMP and then use MRCEPA(0) if MRMP fails. A problem with this scheme is in detecting whether the MRMP fails. Convergence problems in MRMP may be hard to detect at low orders. Inspection of the coefficients in $\Psi_1$ and the singles-doubles part of $\Psi_2$ should be helpful. When in doubt the convergence of the series should be tested.

7.1 Future developments

At the 9th International Conference on Quantum Chemistry (Atlanta, 1997) Morokuma explained that quantum chemistry has come a long way. Along this way a number of landmarks were passed, cf. [2]. These include the introduction of Slater determinants [3], the Hartree-Fock method [4,5], the use of Gaussian basis functions [6], the Roothaan parametrisation of the wavefunction [7], the generalisation of Hartree-Fock to the multi-configuration case [8], the development of multi-reference approaches like MRCI [9,10], and multi-reference perturbation theory (MRPT) [11,12]. The multi-reference coupled
cluster (MRCC) method is underway. Finally, relativistic effects are being included in many codes, and much effort is being invested in coupling quantum-mechanical and classical models. Although this all seems very well it does not mean that we have come to the end of the road.

Looking at approaches to obtain a reasonable estimate of the correlation energy we find that there is a problem with all of them. For example MRCI is not size consistent, MRPT and MRCC may be hampered by divergences [13], and MRCI and MRCC are computationally expensive. Besides these problems, multi-reference methods in general have a tendency to lead to such large configuration spaces that they may not be applicable to large molecules without severe approximations. However, it is well known that dynamical correlation energy has to be accounted for to some extent. MCHF is insufficient to calculate potential energy surfaces accurate enough for qualitatively correct chemical predictions. At this stage the fundamental problem seems to be that everything that can be done using a determinantal basis has been tried, but the results are not really satisfactory.

Basically the paths that lead onwards lay within two extremes. The first extreme is to use the knowledge we have obtained so far and to develop approaches that allow to direct the computational power we have available to the heart of the problems of interest. Mainly this is a matter of tailoring the current methods to allow more flexibility in defining problems. For example, one may want to use MRCI to account for electron correlation in only a part of a molecule. In such a case localisation of orbitals, selections of orbitals and configurations, use of a different basis set for the MCHF calculation and the correlation treatment, and other advanced approximations will be needed. The basic methods will be the same but the new developments will be in defining meaningful approximations.

An other extreme is to develop methods that extend the current approaches to non-determinantal wavefunctions. This is not new as ventures in this direction were already performed by Hylleraas [14]. However, up to a few years ago there was always the promise that new many-configuration methods would cure the problems at hand. I think that is no longer true. This perspective suggests that the time has come to reconsider whether Slater determinants are a good idea. Essentially one would like to have an ab initio method (in contrast to DFT) that accounts for a significant part of the correlation energy while not being more involved than MCHF. This suggests to consider geminal type approaches to
MCHF of some sort. There have been some investigations on the use of geminals in many-configurational methods (cf. [15-28]) but the computational complexity limited their use. Recently, Persson et al. [29] proposed a new way to expand the electron interaction that will reduce the costs of these approaches considerably. Introducing explicitly correlated wavefunctions into MCHF type calculations may be an efficient alternative in describing potential energy surfaces.

In practice of course the final solution will be somewhere in between these extremes. For the next decade I think significant contributions to the latter approach may be expected. Thus although quantum chemistry has come a long way, it may still have a long way to go.

References