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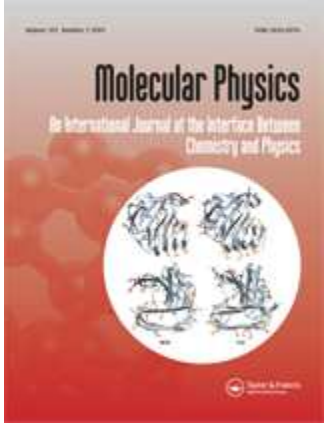

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Many-body Brillouin-Wigner second order perturbation theory: An application to the autoaromatization of hex-3-ene-1,5-diyne (the Bergman reaction)

P. Papp[1], P. Neogrady[2], P. Mach[1], J. Pittner[3], I. Hubač[1,4], and S. Wilson[1,5] *

[1] *Department of Chemical Physics, Faculty of Mathematics and Physics, Comenius University, 842 15 Bratislava, Slovakia*

[2] *Department of Physical and Theoretical Chemistry, Faculty of Natural Sciences, Comenius University, 84215 Bratislava, Slovakia*

[3] *J. Heyrovský Institute of Physical Chemistry, Academy of Sciences of the Czech Republic, Dolejškova 3, 18223 Prague 8, Czech Republic*

[4] *Insitute of Physics, Silesian University, 74601 Opava, Czech Republic*

[5] *Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford OX1 3QZ, England*

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Abstract

The multireference, state specific, second order, Brillouin-Wigner perturbation theory is applied to the autoaromatization of hex-3-ene-1, 5-diyne, the Bergman reaction. Calculations are reported for the reactant (hex-3-ene-1, 5-diyne), the transition state and the product (1, 4-didehydrobenzene). *A posteriori* modifications are made which, in the

*Corresponding author: *quantumsystems@gmail.com*

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case of a single reference function, recover the well known formula of second order many-body perturbation theory, *i.e.* Møller-Plesset *(MP2)* theory, and in the multireference case can be shown to be equivalent to *state-specfic* multireference Rayleigh-Schrödinger-*like* perturbation theory. Calculations are performed for a sequence of correlation consistent basis sets and, by extrapolation, complete basis set limits of the energetics of the Bergman reaction are estimated.

1 Introduction

The importance of many-body methods in the study of molecular systems is now well established. Many chemical processes involve small energy changes which can be masked by employing theoretical description which fail to take account of the many-body character of the system. Many-body electronic structure methods [1] are formulated so as to ensure that the energy scales linearly with the number of electrons in the systems. Such methods avoid the occurrence of spurious nonlinear terms, terms which are associated with unlinked diagrams in diagrammatic formalisms.

Many-body methods are well understood for molecular systems and processes which can be adequately described by a single determinant reference function. A range of perturbative [2] and cluster expansions [3] are available for the theoretical description of such systems. Such methods are robust and are to found in many quantum chemistry program packages, *e.g.* GAUSSIAN [4], MOLCAS [5] and GAMESS [6, 7].

Unfortunately, many molecular species and processes are not adequately described by a single determinantal reference function and demand a multireference formulation. **Multireference many-body perturbation theory was first developed in a seminal paper by Brandow published in 1967 [8]. Brandow employed Brillouin-Wigner perturbation theory in his derivation of a multireference many body (Rayleigh-Schrodinger) perturbation expansion for an effective hamiltonian which is diagonalized in the final stage of any application.** Such formulations are not robust principally because of the so-called intruder state problem[1] caused by changes in the relative ordering of states as the expansion for the correlation energy is developed. **Of course, the intruder state problem can be strongly influenced by the choice of reference function.**

Over the past ten years, state specific methods have been developed which avoid the intruder state problem by considering a single state using a multireference formalism. One of the most promising of these approaches is based on the use of Brillouin-Wigner expansions [12–14]. Historically, Brillouin-Wigner methods [15–17] have been regarded [18–21] as unsuitable for many-body sys-

[1]The intruder state problem has been discussed by many authors. We mention two recent studies: one by Paldus and Li [9] on the intruder state problem in state-universal coupled cluster theory and the other by Perrine *et al* [10] on quadratic Padé approximants and the intruder state problem in multireference perturbation methods. The intruder state problem has also been studied in the nuclear physics literature (e.g. [11]).

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tems containing the exact energy in denominator factors which destroys their extensivity. However, it has been recognized [22] recently that Brillouin-Wigner expansions can be subjected, *a posteriori*, to modification so as to obtain a fully many-body theory [23]. **Whereas Brandow used Brillouin-Wigner methodology to achieve his theoretical derivation of a multireference many-body perturbation expansion, in the more recent work the Brillouin-Wigner approach has been exploited in both the theoretical and computational components of a state specific formulation.**

Second order many-body perturbation theory is the most widely used approach [24] to the electron correlation problem in contemporary *ab initio* molecular electronic structure studies. For systems which are well described by a single determinantal reference functions, this theory, which is based on the use of Rayleigh-Schrödinger perturbation theory to describe electron correlation corrections to the Hartree-Fock independent electron model, affords a robust approach which combines accuracy with computational efficiency. The method, which was first developed by Møller and Plesset [25] in 1934, is often designated *"MP2"* (or *"MBPT2"*), is based on the lowest order of the many-body perturbation theory expansion to take account of correlation effects.

Given the success of *"MP2"* theory for problems for which a single reference function is appropriate, it is important to determine the extent to which the corresponding Brillouin-Wigner method is applicable in a *state specific* formulation with *a posteriori* modification to problems which demand to use of a multireference approach [26]. In a previous paper [27], a comparison of (single reference) MP2 and (multireference) second order modified Brillouin-Wigner calculations has been reported for the dissociation of the first-row diatomic hydride molecules BH and FH using basis sets for which the corresponding full configuration interaction calculations can be carried out.

There have been numerous attempts to develop a robust, multireference many-body perturbation theory for the description of electron correlation effects in molecules. (For reviews, see, for example, Lindgren and Morrison [19], Mukherjee and Pal [28], Hirao [29], Paldus and Li [3, 30], Kaldor [31], Piecuch and coworkers [32, 33], Hubač and Wilson [12, 13].)

Most published formulations employ Rayleigh-Schrödinger perturbation theory in a "perturb then diagonalize" approach, *i.e.* an effective Hamiltonian is first perturbed and then diagonalized. Rayleigh-Schrödinger perturbation theory is favoured because Brueckner's seminal work [34] established the many-body perturbation theory for a single reference function by demonstrating the mutual cancellation of terms corresponding to "unlinked diagrams" in each order of the Rayleigh-Schrödinger expansion. "Perturb then diagonalize" approaches are preferred to "diagonalize then perturb" formulations since, by employing a complete active space, the first approach ensures that the "many-body" character of the theory is not destroyed, *i.e.* terms which scale non-linearly with the number of electrons are not introduced in the diagonalization of the effective Hamiltonian matrix. We shall not provide a detailed review of the many

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formulations of the multireference perturbation theory here[2], but, in section 2, we shall emphasize the particular advantages of our Brillouin-Wigner-based formalism in comparision with other multireference approaches.

In this paper, we apply multireference Brillouin-Wigner many-body theory in second order to the Bergman reaction [36–38], that is the autoaromatization of hex-3-ene-1, 5-diyne to form the singlet *p*-benzyne biradical, 1, 4-didehydrobenzene. Although our primary purpose in this paper is to demonstrate the application of second order, multireference Brillouin-Wigner perturbation theory, the particular reaction studied is an important one upon which the present work provides an alternative theoretical perspective.

The Bergman reaction has been studied extensively over the last decade becoming a useful synthetic reaction [39–45]. The biradical structure, which results from the cycloaromatization reaction, has been shown [46–48] to be a potent antitumour agent through its interaction with DNA strands. 1, 4-didehydrobenzene is responsible for the oxidative DNA cleavage. It extracts hydrogen from the saccharide phosphate backbone to form benzene, denaturing the DNA and ultimately causing cell death.

The enediynes were revealed as a new class of antitumour antibiotics in 1987 (for a review see [49]). Calicheamicin γ_1^I [50] and esperamicin A_1 [51] are representative of the first two sub-classes to be recognised as such, the calicheamicins and esperamicins. The neocarzinostatin chromophore [52], although previously identified, was only later recognised as an enediyne antibiotic because of the similarity of its mode of action. In 1989, dynemicin A [53] was reported as the first of a new series of enediynes, the dynemicins. These compounds display extremely potent antitumour activity. The enediyne moiety is attached to a molecular template which is responsible for the distribution of the drug inside the organism and/or the initiation of the reaction. The enediyne-like structure is often strained in the complex molecule resulting in a lowering of the reaction energy and energy barrier so that the Bergman reaction may be induced photochemically and thermally [54, 55], or by changes in the environment, such as pH value. Enediynes are characterized by a nine- or 10-membered ring containing two triple bonds separated by a double bond. The enediyne group readily cyclizes via a diradical intermediate that cleaves DNA, giving rise to enediynes' powerful antitumor activity.

The energetics of the Bergman reaction determines the conversion rate of the drug from its inactive closed-shell form to its active biradical form, which in turn defines the kinetics of the reaction sequence once the drug is activated. In 1994, Roth, Hopf and Horn [56] characterized the Bergman reaction and its barrier enthalpies by *p*-benzyne trapping rates. They reported a reaction enthalpy of 8.5 ± 1 kcal mol^{-1} at 298°K and an activation enthalpy of 28.2 ± 0.5 kcal mol^{-1} at 470°K. From studies of the reaction by collision-induced dissociation, Wenthold and Squires [57] reported a reaction enthalpy of 13 ± 3 kcal mol^{-1} at 298°K.

[2] **In a recent paper, Chaundhuri *et al* [35] provide an appraisal of multireference perturbation theories based on benchmark calculations for a number of small molecules.**

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In the next section, we consider the theoretical description of the autoaromatization of hex-3-ene-1,5-diyne with particular emphasis on Brillouin-Wigner-based methods. In section 3, we described the computational approach employed in the present study - the basis sets employed, the algorithms and quantum chemistry programs used. A sequence of basis sets is employed so that the convergence of the calculated energies with respect to basis set can be monitored and extrapolation to the complete basis set limit attempted. Our results are presented in section 4 and the convergence of the calculated energy values with respect to basis set analyzed. Section 5 contains our discussion and conclusions, and includes a comparison with previous theoretical studies of the Bergman reaction.

2 Theoretical description of the autoaromatization of hex-3-ene-1,5-diyne

This system, which has the formula C_6H_4, contains 40 electrons, 12 "core" electrons and 28 "valence" electrons. The molecular structures involved in the Bergman reaction are shown in Figures 1, 2 and 3. In Figure 1, the reactant, labelled r, is hex-3-ene-1, 5-diyne. It has $\mathsf{C_{2v}}$ point group symmetry and contains two C-C bonds, one C=C bond, and two C≡C, together with four C-H bonds. The ring closure process is assumed to follow a reaction path within $\mathsf{C_{2v}}$ symmetry. Figure 2 shows the transition state, t, in which the two triple bonds are replaced by two double bonds and four unpaired electrons. Finally, Figure 3 shows the product p, the singlet *para*-benzyne biradical, which contains four C-C single bonds and two C=C together with two unpaired electrons. It has a higher point group symmetry than the reactant, namely $\mathsf{D_{2h}}$. The Bergman reaction involves the transformation of two single, one double and two triple carbon-carbon bonds formally into six benzene bonds. Theoretical methods employed to describe this reaction must achieve a balanced description of the structures involved. Such methods must describe the near degeneracy effects which arise during of bond breaking and formation. They must also provide an adequate description of dynamic correlation effects.

Over the past decade, several theoretical studies of the Bergman reaction have been reported [58–76]. The biradical 1, 4-didehydrobenzyne has a multireference character caused by a low-lying virtual orbital. Electron correlation treatments based on a single reference function are therefore inadequate basis for the theoretical description of the Bergman cyclization reaction. Thus, for example, Lindh and Schutz [62] points out that "the CCSD(T) method is inappropriate for the study of the Bergman reaction". In recent work, Puiggros *et al.* [76] published a study of the Bergman reaction in which the Brillouin-Wigner formalism was employed in multireference coupled cluster and configuration interaction studies. These authors used coupled cluster expansion with single and double excitations, designated MR-BWCCSD, and double excitation configuration interaction, designated MR-BWCID.

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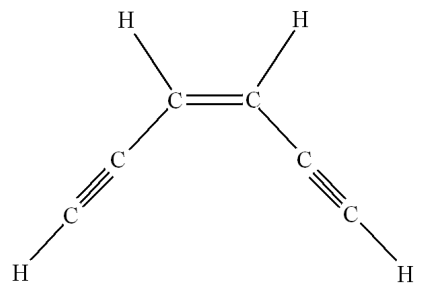

Figure 1: The reaction molecule, r, hex-3-ene-1, 5-diyne.

In this paper, we used multireference second order Brillouin-Wigner perturbation theory, which we designate BW2, to study the Bergman cyclization reaction. An *a posteriori* modification is applied to the second order Brillouin-Wigner energy which ensures that a value equivalent to the second order Rayleigh-Schrödinger energy is obtained. In this way, our calculations may be viewed as state specific, multireference second order Rayleigh-Schrödinger-*like* perturbation theory.

Below details of the multireference functions employed in the present study of the Bergman reactionare given in section 2.1. In section 2.2 the many-body Brillouin-Wigner formalism is presented. The second order multireference Brillouin-Wigner perturbation theory is described in section 2.3. Finally, in section 2.4, an *a posteriori* modification is introduced to recover a fully many-body formalism.

2.1 Multireference functions for the Bergman reaction

The use of multireference functions in electron correlation energy studies introduces a flexibility which is not present in single reference formalisms. In this work, we follow Puiggros *et al* [76] and use two configuration functions for the reactant, transition state and the product. **This facilitates a numerical comparison with the Brillouin-Wigner coupled cluster results reported by Puiggros *et al.* In this subsection, we define the two-configuration functions used here. We use the canonical Hartree-Fock orbitals and the zero-order Hamiltonian is taken to be the Hartree-Fock operator for the ground state. There would be no difficulty, in principle, if we were to employ, for example, the CAS-SCF (complete active space self-consistent field) orbitals.**

The 40-electron C_6H_4 system can be described by a Slater determinant constructed from 20 spin orbitals for those geometries for which a single reference

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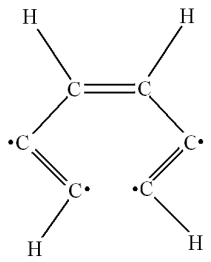

Figure 2: The transition state, t.

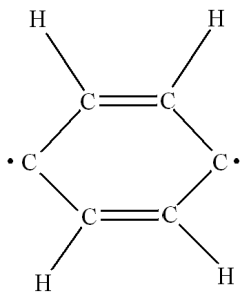

Figure 3: The product molecule, p, $1,4$-didehydrobenzyne.

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function is appropriate. However, the theoretical description of the Bergman reaction demands the use of a two configuration reference, the first configuration being the (matrix) Hartree-Fock function with the second obtained by a double electron replacement from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

From our calculations for the reactant, the single determinant Hartree-Fock function has the form

$$\Phi_0^r = \left|1a_1^2 1b_2^2 2b_2^2 2a_1^2 3a_1^2 3b_2^2 4a_1^2 4b_2^2 5a_1^2 5b_2^2 6a_1^2 6b_2^2 7a_1^2 8a_1^2 7b_2^2 1b_1^2 1a_2^2 9a_1^2 8b_2^2 2b_1^2\right| \quad (1)$$

This single reference function is capable of describing the reactant, hex-3-ene-1, 5-diyne, but, since the transition state and the product, *para*-benzyne, are expected to have significant multireference character, and we require a balanced description of the reaction, a second configuration written as

$$\Phi_1^r = \left|1a_1^2 1b_2^2 2b_2^2 2a_1^2 3a_1^2 3b_2^2 4a_1^2 4b_2^2 5a_1^2 5b_2^2 6a_1^2 6b_2^2 7a_1^2 8a_1^2 7b_2^2 1b_1^2 1a_2^2 9a_1^2 8b_2^2 2a_2^2\right| \quad (2)$$

was included in the reference function by a double electron replacement from the $2b_1$ molecular orbital to the $2a_2$ orbital.

For the transition state, the two configurations included in the reference function have the form:

$$\Phi_0^t = \left|1a_1^2 2a_1^2 1b_2^2 2b_2^2 3b_2^2 3a_1^2 4a_1^2 4b_2^2 5a_1^2 5b_2^2 6a_1^2 6b_2^2 7a_1^2 8a_1^2 7b_2^2 1b_1^2 9a_1^2 1a_2^2 2b_1^2 8b_2^2\right| \quad (3)$$

and

$$\Phi_1^t = \left|1a_1^2 2a_1^2 1b_2^2 2b_2^2 3b_2^2 3a_1^2 4a_1^2 4b_2^2 5a_1^2 5b_2^2 6a_1^2 6b_2^2 7a_1^2 8a_1^2 7b_2^2 1b_1^2 9a_1^2 1a_2^2 2b_1^2 10a_1^2\right| \quad (4)$$

where Φ_1^t is obtained by a double electron replacement from the $8b_2$ molecular orbital in Φ_0^t by a $10a_1$ orbital.

Finally, for the product, the reference functions was constructed from the following two configurations

$$\begin{aligned}\Phi_0^p &= \left|1a_g^2 1b_{2u}^2 1b_{1u}^2 1b_{3g}^2 2b_{1u}^2 2a_g^2 3a_g^2 2b_{2u}^2 3b_{1u}^2 2b_{3g}^2 4a_g^2 5a_g^2 4b_{1u}^2 3b_{2u}^2 4b_{2u}^2 3b_{3g}^2 1b_{3u}^2\right. \\ &\quad \left. 1b_{1g}^2 1b_{2g}^2 5b_{1u}^2\right| \quad (5)\end{aligned}$$

$$\begin{aligned}\Phi_1^p &= \left|1a_g^2 1b_{2u}^2 1b_{1u}^2 1b_{3g}^2 2b_{1u}^2 2a_g^2 3a_g^2 2b_{2u}^2 3b_{1u}^2 2b_{3g}^2 4a_g^2 5a_g^2 4b_{1u}^2 3b_{2u}^2 4b_{2u}^2 3b_{3g}^2 1b_{3u}^2\right. \\ &\quad \left. 1b_{1g}^2 1b_{2g}^2 6a_g^2\right| \quad (6)\end{aligned}$$

the second function being obtained by replacing the $5b_{1u}$ molecular orbital by the $6a_{1g}$ orbital.

The two-configuration reference spaces defined above $\{\Phi_0^r, \Phi_1^r\}$, $\{\Phi_0^t, \Phi_1^t\}$ and $\{\Phi_0^p, \Phi_1^p\}$ provide a balanced description of the reactant, transistion state and product. They do not provide a continuous description along the reaction coordinate. These configurations were employed in the Brillouin-Wigner coupled cluster theory study of the Bergman reaction reported by Puiggros *et al* [76] with which the present calculations are compared.

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2.2 Many-body Brillouin-Wigner formalism

Many-body Brillouin-Wigner methods form the basis of a robus approach to the electron correlation problem in cases where a multireference formalism is required. The reference energy in Brillouin-Wigner perturbation theory may be described as "fully dressed" [77]. This characteristic allows the intruder state problem to be avoided and rapid convergence of the perturbation expansion achieved.

The following presentation serves *(i)* to provide the necessary background, *(ii)* to introduce our notation, and *(iii)* to describe the unique advantages of the Brillouin-Wigner approach in studies of the correlation problem for systems requiring a multireference formalism. We have noted above that the Brillouin-Wigner perturbation expansion was employed by Brandow [8] as an intermediate step in his derivation of a multireference many-body perturbation theory based on the Rayleigh-Schrödinger expansion. Like other multireference methods based on Rayleigh-Schrödinger theory, the Brandow approach is susceptable to the intruder state problem. In the many-body Brillouin-Wigner theory advocated in the present work, calculations are carried out in the Brillouin-Wigner formalism and then *a posteriori* modification is made to recover a fully many-body theory. A more detailed description of the many-body Brillouin-Wigner formalism can be found elsewhere [12–14].

We seek to approximate the solutions of the time-independent electronic Schrödinger equation associated with the Hamiltonian $\mathcal{H}$, which may be written

$$\mathcal{H}\Psi_k = \mathcal{E}_k\Psi_k; \quad k = 0, 1, 2, ... \tag{7}$$

where $\mathcal{E}_k$ is the exact eigenvalue for the state k and Ψ_k is the corresponding eigenfunction. As is usual, perturbation theory is developed by writing the total Hamiltonian, $\mathcal{H}$, as a sum of two parts, *i.e.*

$$\mathcal{H} = \mathcal{H}_0 + \lambda\mathcal{H}_1 \tag{8}$$

where $\mathcal{H}_0$ is the zero-order Hamiltonian and $\mathcal{H}_1$ is the perturbation operator. λ is the perturbation parameter which interpolates between the reference model when $\lambda = 0$ and the perturbed problem when $\lambda = 1$.

It is assumed that the solutions of the zero-order eigenproblem

$$\mathcal{H}_0\Phi_k = E_k\Phi_k, \quad k = 0, 1, 2, ... \tag{9}$$

are known. In practice, of course, the solutions of the eigenproblem (9) are known within the *algebraic approximation* realized by some choice of finite basis set in terms of which the single particle state functions are parametrized. It is only by employing a sequence of related finite basis sets that the exact solutions of (9) can be approached and/or extrapolation to the basis set limit attempted. Let $\mathcal{S}$ be the set of all Φ_k arising from the solution of (9).

In general, we let

$$\{\Phi_k;\ k = 0, 1, 2, ...p - 1\} \tag{10}$$

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be a subset of linearly independent functions which constitute the *reference space*, which we label $\mathcal{P}$. The choice of the functions included in $\mathcal{P}$ is dictated by the nature of the problem under investigation. For the present study, $\mathcal{P}$ is determined by the appropriate choice of reference function as described in section 2.1.

Let P be the projection operator onto the reference space $\mathcal{P}$:

$$P = \sum_{j \in \mathcal{P}} |\Phi_j\rangle \langle \Phi_j| \tag{11}$$

and let Q be its orthogonal complement, which projects on to the space $\mathcal{Q}$

$$Q = I - P = \sum_{j \notin \mathcal{P}} |\Phi_j\rangle \langle \Phi_j| \,. \tag{12}$$

P and Q satisfy the idempotency and orthogonality relations

$$P^2 = P \qquad Q^2 = Q \qquad PQ = 0 \qquad P + Q = I \tag{13}$$

We can write the space $\mathcal{S}$ as

$$\mathcal{S} = \mathcal{P} \oplus \mathcal{Q} \tag{14}$$

Obviously, the single reference formalism occurs as a special case of the partition of $\mathcal{S}$ defined in (14) in which the subset (10) defining the reference space consists of a single function.

Let us now introduce the projection of the exact wave function, Ψ_k, onto the reference space $\mathcal{P}$, *i.e.*

$$\Psi_k^P = P\Psi_k, \;\; k = 0, 1, 2, ..., p-1 \tag{15}$$

Ψ_k^P is sometimes called the *model function*. The exact wave function can be written in the form

$$\Psi_k = \Psi_k^P + Q\Psi_k, \tag{16}$$

that is, as the sum of a component in the model space and a component in the orthogonal space. Obviously, the model function, Ψ_k^P, can be written as a linear combination of the subset (10) which spans the reference space. Thus we can write

$$\Psi_k^P = \sum_{j \in \mathcal{P}} C_{jk} \Phi_j \tag{17}$$

where C_{jk} is a coefficient which, at this stage, is undetermined. The functions Ψ_k^P are, in general, non-orthogonal but are assumed to be linearly independent.

Using the Hamiltonian operator in the form(8), we can write the exact Schrödinger equation, equation (7) as

$$(\mathcal{H}_0 + \lambda \mathcal{H}_1)|\Psi_k\rangle = \mathcal{E}_k |\Psi_k\rangle \tag{18}$$

This equation can then be rearranged to the following form:

$$(\mathcal{E}_k - \mathcal{H}_0)|\Psi_k\rangle = \lambda \mathcal{H}_1 |\Psi_k\rangle. \tag{19}$$

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Multiplying this equation from the left by the projection operator Q, we obtain

$$(\mathcal{E}_k - \mathcal{H}_0)Q|\Psi_k\rangle = \lambda Q\mathcal{H}_1|\Psi_k\rangle. \tag{20}$$

We now develop a series expansion for Ψ_k by first introducing the Brillouin-Wigner type resolvent $\mathcal{B}_k$ which satisfies the equation

$$\mathcal{B}_k(\mathcal{E}_k - \mathcal{H}_0) = Q \tag{21}$$

and then multiplying equation (20) from the left by $\mathcal{B}_k$ to give

$$\mathcal{B}_k(\mathcal{E}_k - \mathcal{H}_0)Q\,|\Psi_k\rangle = \lambda\mathcal{B}_k Q\mathcal{H}_1\,|\Psi_k\rangle \tag{22}$$

Using equation (21) we immediately obtain

$$Q\,|\Psi_k\rangle = \lambda\mathcal{B}_k\mathcal{H}_1\,|\Psi_k\rangle \tag{23}$$

whereupon, by substituting in equation (16), we have the required result

$$|\Psi_k\rangle = \left|\Psi_k^P\right\rangle + \lambda\mathcal{B}_k\mathcal{H}_1\left|\Psi_k^P\right\rangle. \tag{24}$$

which is the Brillouin-Wigner recursion for the exact wave function.

Explictly, the exact wavefunction, Ψ_k, is expanded as follows

$$\Psi_k = \left(1 + \lambda\mathcal{B}_k\mathcal{H}_1 + \lambda^2\mathcal{B}_k\mathcal{H}_1\mathcal{B}_k\mathcal{H}_1 + \lambda^3\mathcal{B}_k\mathcal{H}_1\mathcal{B}_k\mathcal{H}_1\mathcal{B}_k\mathcal{H}_1 + ...\right)\Psi_k^P \tag{25}$$

where $\mathcal{B}_k$, the Brillouin-Wigner type propagator, can be written in sum-over-states form

$$\mathcal{B}_k = \sum_{j\notin P}\frac{|\Phi_j\rangle\langle\Phi_j|}{\mathcal{E}_k - E_j} \tag{26}$$

which depends on the unknown exact energy eigenvalue $\mathcal{E}_k$. It is this dependence of $\mathcal{E}_k$ which characterizes Brillouin-Wigner methods.

Without any loss of generality, the exact wavefunction, Ψ_k, and the model function, Ψ_k^P, may be taken to satisfy the following intermediate normalization conditions

$$\begin{aligned}\left\langle\Psi_k^P \mid \Psi_k\right\rangle &= 1\\ \left\langle\Psi_k^P \mid \Psi_k^P\right\rangle &= 1\end{aligned} \tag{27}$$

Thus the model function is normalized and the overlap between the model function and the exact wave function is set to unity.

Now we are ready to introduce the wave operator, Ω_k, which is defined by

$$|\Psi_k\rangle = \Omega_k\left|\Psi_k^P\right\rangle. \tag{28}$$

Application of the wave operator to the model function yields the exact wave function. We recall that application of the projection operator P to the exact wave function yields the model function. Comparing (28), which defines the

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wave operator, with the Brillouin-Wigner expansion for the exact wave function (25), we see immediately that the wave operator can be written as

$$\Omega_k = P + \lambda\mathcal{B}_k\mathcal{H}_1 + \lambda\mathcal{B}_k\mathcal{H}_1\mathcal{B}_k\mathcal{H}_1 + \lambda\mathcal{B}_k\mathcal{H}_1\mathcal{B}_k\mathcal{H}_1\mathcal{B}_k\mathcal{H}_1 + ... \tag{29}$$

Equation (29) can be re-written as the recursion,

$$\Omega_k = P + \lambda\mathcal{B}_k\mathcal{H}_1\Omega_k, \tag{30}$$

which may be seen to be the Bloch equation [78] in Brillouin-Wigner form. Equation (29) is exact and is fully equivalent to the Schrödinger equation (7) in the reference space. However, it is more suitable for generating the Brillouin-Wigner expansion. It should be emphasized that equation (30) defines a *state-specific* wave operator.

We are now ready to introduce the "effective" Hamiltonian which acts only in the reference subspace $\mathcal{P}$

$$\mathcal{H}_k = P\mathcal{H}\Omega_k P \tag{31}$$

Although the effective Hamiltonian, $\mathcal{H}_k$, operates only in the reference space $\mathcal{P}$, it has the exact energy, $\mathcal{E}_k$, as an eigenvalue, *i.e.*

$$\mathcal{H}_k\Psi_k^P = \mathcal{E}_k\Psi_k^P \tag{32}$$

Using the partition of the Hamiltonian into a reference Hamiltonian and a perturbation given in equation (8), we can write the effective Hamiltonian operator (31) in the form

$$\mathcal{H}_k = P\mathcal{H}_0P + \lambda P\mathcal{H}_1\Omega_k P \tag{33}$$

which can then be re-written in the alternative form

$$\mathcal{H}_k = P\mathcal{H}_0P + \lambda P\mathcal{V}_k P, \quad k = 0, 1, 2, ..., p-1 \tag{34}$$

In equation (34) we have introduced the reaction operator, $\mathcal{V}_k$, which is defined as the following operator product

$$\mathcal{V}_k = \mathcal{H}_1\Omega_k \tag{35}$$

Combining the Bloch equation (30) with the definition of the reaction operator (35) gives a Lippmann-Schwinger-*like* equation [79] in Brillouin-Wigner form

$$\mathcal{V}_k = \mathcal{H}_1P + \lambda\mathcal{H}_1\mathcal{B}_k\mathcal{V}_k \tag{36}$$

It should be emphasized that, in the Brillouin-Wigner form, the reaction operator, $\mathcal{V}_k$, is a *state specific* operator corresponding to only one eigenenergy $\mathcal{E}_k$. Equation (36) is also exact and equivalent to the Schrödinger equation (7), but is more suitable for generating Brillouin-Wigner expansions.

Let us briefly consider the relation between the *state specific* wave operators and reaction operators defined above for multireference Brillouin-Wigner theory and the corresponding operators in the multireference Rayleigh-Schrödinger

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perturbation theory. It should also be emphasized that the wave operator arising in the multireference Rayleigh-Schrödinger formalism, Ω can be related to the wave operators Ω_k in the Brillouin-Wigner method through the relation

$$\Omega = \sum_{k=0}^{p-1} \Omega_k P_k \tag{37}$$

Ω can be applied to all states in the model space. On the other hand, Ω_k can only be applied to the state labelled k. In the Brillouin-Wigner formalism, there is a *different* wave operator for each state. (There is a similar relation between the reaction operators in Brillouin-Wigner and Rayleigh-Schrödinger theories.) Consequently, in the Brillouin-Wigner approach, the exact energies, $\mathcal{E}_k$, are eigenvalues of *different* effective hamiltonian operators

$$\mathcal{H}_k \Psi_k^P = \mathcal{E}_k \Psi_k^P, \quad k = 0, 1, 2, ..., p-1 \tag{38}$$

In the multireference Rayleigh-Schrödinger formalism, the exact energies are eigenvalues of a *common* effective hamiltonian operator.

2.3 Multireference Brillouin-Wigner perturbation theory through second order

Given the multireference functions defined in section 2.1, second-order Brillouin-Wigner perturbation theory with an *a posteriori* modification can be used to describe dynamic correlation effects. In this subsection, we consider the second order, multireference Brillouin-Wigner perturbation theory. In subsection 2.4, we recover a *many-body* Brillouin-Wigner perturbation theory through second order by introducing an *a posteriori* modification term. The second order theory represents the lowest order for the description of correlation effects and, for a well chosen reference function, it can be anticipated that the second order theory should account for a substantial fraction of the electron corrleation energy.

Let us consider the general case of a p-state system and obtain an explicit formulation of the multireference Brillouin-Wigner second order perturbation theory for this case. In the calculations reported in this work the reference space contains only two functions, *i.e.* $p = 2$. In the p-state case, we have a reference space spanned by p orthonormal N particle functions, $\Phi_0, \Phi_1, ..., \Phi_{p-1}$. The projection operator onto this space is defined as follows:

$$P = \sum_{j=0}^{p-1} |\Phi_j\rangle \langle\Phi_j| \tag{39}$$

The model functions are given by equation (15) and the corresponding wave operators, defined by equation (28), are written

$$\Omega_0, \Omega_1, ..., \Omega_{p-1} \tag{40}$$

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The corresponding reaction operators, defined by equation (35), are written

$$\begin{aligned} \mathcal{V}_0 &= \mathcal{H}_1\Omega_0 \\ \mathcal{V}_1 &= \mathcal{H}_1\Omega_1 \\ ... & \\ \mathcal{V}_{p-1} &= \mathcal{H}_1\Omega_{p-1} \end{aligned} \tag{41}$$

The effective Schrödinger equation for the state k has the form

$$\mathcal{H}_k\Psi_k^P = \mathcal{E}_k\Psi_k^P, \quad k = 0, 1, ..., p-1 \tag{42}$$

The effective Hamiltonian operator for this state specific formalism can be written as

$$\begin{aligned} \mathcal{H}_k &= P\mathcal{H}\Omega_k P \\ &= P\mathcal{H}_0 P + P\mathcal{H}_1\Omega_k P \\ &= P\mathcal{H}_0 P + P\mathcal{V}_k P \end{aligned} \tag{43}$$

Using the expansions (39), the operator (43) can be written more explicitly as

$$\begin{aligned} \mathcal{H}_k &= \{\sum_{j=0}^{p-1} |\Phi_j\rangle\langle\Phi_j|\}\mathcal{H}_0\{\sum_{j=0}^{p-1} |\Phi_j\rangle\langle\Phi_j|\} \\ &\quad +\{\sum_{j=0}^{p-1} |\Phi_j\rangle\langle\Phi_j|\}\mathcal{V}_k\{\sum_{j=0}^{p-1} |\Phi_j\rangle\langle\Phi_j|\} \end{aligned} \tag{44}$$

For the state $k = \alpha$, we have a model function Ψ_α^P, which is given by

$$\Psi_\alpha^P = \sum_{j=0}^{p-1} C_j^\alpha \Phi_j \tag{45}$$

The coefficients C_j^α are obtained by solution of the secular equation which, for the state α, can be written in the form

$$\begin{pmatrix} \langle\Phi_0|\mathcal{H}_\alpha|\Phi_0\rangle - \mathcal{E}_\alpha & \langle\Phi_0|\mathcal{V}_\alpha|\Phi_1\rangle & ... & \langle\Phi_0|\mathcal{V}_\alpha|\Phi_{p-1}\rangle \\ \langle\Phi_1|\mathcal{V}_\alpha|\Phi_0\rangle & \langle\Phi_1|\mathcal{H}\alpha|\Phi_1\rangle - \mathcal{E}_\alpha & ... & \langle\Phi_1|\mathcal{V}_\alpha|\Phi_{p-1}\rangle \\ ... & ... & ... & ... \\ \langle\Phi_{p-1}|\mathcal{V}_\alpha|\Phi_0\rangle & \langle\Phi_{p-1}|\mathcal{V}_\alpha|\Phi_1\rangle & ... & \langle\Phi_{p-1}|\mathcal{H}_\alpha|\Phi_{p-1}\rangle - \mathcal{E}_\alpha \end{pmatrix} \times \begin{pmatrix} C_0^{(\alpha)} \\ C_1^{(\alpha)} \\ ... \\ C_{p-1}^{(\alpha)} \end{pmatrix} = 0 \tag{46}$$

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The matrix elements of the effective Hamiltonian are given in sum-over-states form as

$$\langle\Phi_i|\,\mathcal{V}_\alpha\,|\Phi_j\rangle = \langle\Phi_i|\,\mathcal{H}_1\,|\Phi_j\rangle + \sum_{m\notin P}\frac{\langle\Phi_i|\,\mathcal{H}_1\,|\Phi_m\rangle\,\langle\Phi_m|\,\mathcal{V}_\alpha\,|\Phi_j\rangle}{\mathcal{E}_\alpha - E_m} \tag{47}$$

and the diagonal elements are given by the expression

$$\langle\Phi_i|\,\mathcal{H}\alpha\,|\Phi_i\rangle = \langle\Phi_i|\,\mathcal{H}_0\,|\Phi_i\rangle + \langle\Phi_i|\,\mathcal{V}_\alpha\,|\Phi_i\rangle \tag{48}$$

with $i, j = 0, 1, ..., p-1$. It should be noted that, since $\mathcal{H}_1$ is a two-particle operator, the configuration $|\Phi_m\rangle$ is at most a double replacement with respect to $|\Phi_i\rangle$ in (47).

The matrix elements of the reaction operator, $\mathcal{V}_\alpha$, which are given in (47), are obtained from the Lippmann-Schwinger-*like* equation in sum-over-states form, equation (36). Specifically, we have

$$\langle\Phi_m|\,\mathcal{V}_\alpha\,|\Phi_j\rangle = \langle\Phi_m|\,\mathcal{H}_1\,|\Phi_j\rangle + \sum_{n\notin P}\frac{\langle\Phi_m|\,\mathcal{H}_1\,|\Phi_n\rangle\,\langle\Phi_n|\,\mathcal{V}_\alpha\,|\Phi_j\rangle}{\mathcal{E}_\alpha - E_n}, \quad \forall m \notin \mathcal{P} \tag{49}$$

Equation (46) has p eigenvalues of which we take only one. The exact energy, $\mathcal{E}_\alpha$, occurs in the denominator factors in equations (47) and (49). Equation (46) must, therefore, be solved iteratively until self-consistency is achieved. The corresponding eigenvector defines the model function (45). This energy dependence is a characteristic feature of Brillouin-Wigner methods. In practice, the secular equation (46) is set up and solved to obtain an estimate of $\mathcal{E}_\alpha$ which is then used to reconstruct the effective Hamiltonian matrix. This process is repeated until, if it is convergent, self-consistency is achieved.

If we restrict the order of perturbation admitted in (49) then we realize a finite order multireference Brillouin-Wigner perturbation theory. Specifically, if we neglect terms of order λ^3 and higher we are led immediately to the second order theory for which the matrix elements of the effective Hamiltonian (47) take the form

$$\langle\Phi_i|\,\mathcal{V}_\alpha\,|\Phi_j\rangle = \langle\Phi_i|\,\mathcal{H}_1\,|\Phi_j\rangle + \sum_{m\notin P}\frac{\langle\Phi_i|\,\mathcal{H}_1\,|\Phi_m\rangle\,\langle\Phi_m|\,\mathcal{H}_1\,|\Phi_j\rangle}{\mathcal{E}_\alpha - E_m} \tag{50}$$

Use of (48) and (50) to construct the effective Hamiltonian matrix (46) defines our second order, multireference Brillouin-Wigner perturbation theory. It is this second order theory with which we are concerned in the present study of the Bergman reaction.

2.4 Many-body Brillouin-Wigner perturbation theory through second order

Brillouin-Wigner perturbation theory is not, in general, a true many-body theory in that it contains terms which scale non-linearly with the number of electrons in the system. It is easily shown, for example, that an application of finite

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order Brillouin-Wigner perturbation theory to the model problem of an array of n well-separated He atoms leads to the correlation energy estimate which is not equal to n times that for a single He atom. Often Brillouin-Wigner methods have been regarded [18–21] as unsuitable for the study of many-body systems. However, it has been shown [22] that *a posteriori* modifications to Brillouin-Wigner perturbation theory can be made based on the identity relation [8]

$$(\mathcal{E}_\alpha - E_m)^{-1} = (E_\alpha - E_m)^{-1} + (E_\alpha - E_m)^{-1} (-\Delta E_\alpha) (\mathcal{E}_\alpha - E_m)^{-1} , \quad (51)$$

where $\Delta E_\alpha = \mathcal{E}_\alpha - E_\alpha$, can be applied to the matrix elements in (46). Rearranging the identity relation (51) we have

$$(\mathcal{E}_\alpha - E_m)^{-1} + (E_\alpha - E_m)^{-1} (\Delta E_\alpha) (\mathcal{E}_\alpha - E_m)^{-1} = (E_\alpha - E_m)^{-1} . \quad (52)$$

The first term on the left hand side of (52) is a Brillouin-Wigner denominator and the term on the right hand side is a Rayleigh-Schrödinger denominator. The second term on the left hand side can be regarded as an *a posteriori* removal of unlinked diagram terms from a Brillouin-Wigner expansion. In general, this identity relation is applied *a posterori* so the state specfic multireference Brillouin-Wigner theory avoids convergence problems associated with intruder states but introduces terms which are not extensive, *i.e.* do not scale linearly with particle number, the *a posteriori* modification then removes these terms and restored extensivity so that a true *many-body* theory is recovered.

For the state $k = \alpha$ the "modified" matrix elements obtained after using the identity relation for the p-state case may be written

$$\begin{aligned} \langle \Phi_i | \mathcal{V}_\alpha | \Phi_j \rangle &= \langle \Phi_i | \mathcal{H}_1 | \Phi_j \rangle + \sum_{m \notin P} \frac{\langle \Phi_i | \mathcal{H}_1 | \Phi_m \rangle \langle \Phi_m | \mathcal{V}_\alpha | \Phi_j \rangle}{\mathcal{E}_\alpha - E_m} \\ &\quad + \{ \sum_{m \notin P} \frac{\Delta E_\alpha \langle \Phi_i | \mathcal{H}_1 | \Phi_m \rangle \langle \Phi_m | \mathcal{V}_\alpha | \Phi_j \rangle}{(E_\alpha - E_m)(\mathcal{E}_\alpha - E_m)} \} \end{aligned} \quad (53)$$

Matrix elements of the reaction operator, $\mathcal{V}_\alpha$, could be determined by using (53) including the terms contained in the braces $\{\ldots\}$ *after convergence has been achieved*. However, it can be shown that in the case $p = 1$, *i.e.* the single reference case, equation (53) reduces to the familiar and widely used *"MP2"* expression. In the multireference case, equation (53) is independent of the exact ground state energy, $\mathcal{E}_0$, and becomes

$$\langle \Phi_i | \mathcal{V}_\alpha | \Phi_j \rangle = \langle \Phi_i | \mathcal{H}_1 | \Phi_j \rangle + \sum_{m \notin P} \frac{\langle \Phi_i | \mathcal{H}_1 | \Phi_m \rangle \langle \Phi_m | \mathcal{H}_1 | \Phi_j \rangle}{E_\alpha - E_j} \quad (54)$$

which could be regarded as a Rayleigh-Schrödinger-*like* expression in that the denominator depends only on the unperturbed energies. However, according to Lindgren and Morrison (*p.* 207) [19]

> *"one of the fundamental differences between the Brillouin-Wigner and the Rayleigh-Schrödinger formalisms* [is that in] *the former case*

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there is one effective Hamiltonian for each energy, while in the latter case a single operator yields all the model states and corresponding energies."

and our expression (54) should be viewed, therefore, as a Brillouin-Wigner expression. Certainly, the Brillouin-Wigner expansion described in subsections 2.2 and 2.3 is of central important to the derivation of expression (54). Equation (54) is our working equation and is obviously more efficient in computational implementations than equation (53) which contains the *a posteriori* modification explicitly. In the multireference case, application of the *a posteriori* modification to second order Brillouin-Wigner perturbation theory leads to *state specific* second-order Rayleigh-Schrödinger-*like* perturbation theory. (Note that other formulations of multireference Rayleigh-Schrödinger perturbation theory[3] are not state specific in that the wave operator employed does not depend on the model function on which it operate.)

3 Computational methods

In this section, we describe the computational methods employed in the present study. In section 3.1 details of the finite basis sets used are given. In section 3.2 the specific algorithms invoked in performing the computations are defined together with details of the "standard" quantum chemistry packages utilized in this study.

3.1 Finite basis set approximations

It is well known that the choice of basis set in which the single particle state functions are parametrized ultimately determines the accuracy of a calculation [81]. It is also well established that an estimate of the basis set truncation error in a particular calculation can be estimated by employing a sequence of related basis sets so that convergence of the problem with respect to basis set size can be assessed [81].

In this work, we employed the correlation consistent basis set developed by Dunning and his colleagues [82, 83]. Specifically, we use the sequence of correlation consistent basis sets designated *cc*-pVXZ with X= D, T, Q, has been used, that is "double zeta", "triple zeta" and "quadruple zeta" sets.

To facilitate comparison with the Brillouin-Wigner coupled cluster calculations reported by Puiggros *et al* [76], we employed cartesian Gaussian-type basis functions in the basis set of "double zeta" quality. However, spherical harmonic Gaussian-type functions were used for the larger basis sets.

The "double zeta" (*cc*-pVDZ) basis set for the C atom consists of $9s$, $4p$,$1d$ Gaussian primitive functions contracted to $3s$, $2p$, $1d$ functions, *i.e.* $(9s, 4p, 1d) \rightarrow$

[3] A pedagogical presentation of multireference many-body perturbation theory is given by Kucharski and Bartlett [80].

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$[3s, 2p, 1d]$, whilst for the H atom the primitive set of $4s$, $1p$ functions is contracted to a $2s$, $1p$ set, *i.e.* $(4s, 1p) \rightarrow [2s, 1p]$. The *cc*-pVDZ molecular basis set for the C_6H_4 system contains $26s$, $16p$, $6d$ contracted functions, a total of 110 contracted functions, constructed from a $70s$, $28p$, $6d$ primitive set, a total of 190 primitive functions. As stated in section 2, the ring closure process is assumed to follow a reaction path within C_{2v} point group symmetry. The symmetry adapted basis functions in the *cc*-pVDZ molecular basis set for the C_6H_4 system divide between the irreducible representations of the C_{2v} group as follows: $41a_1$ $41b_1$ $14b_2$ $14a_2$.

The "triple zeta" (*cc*-pVTZ) basis set for the C atom is constructed according to the contraction $(10s, 5p, 2d, 1f) \rightarrow [4s, 3p, 2d, 1f]$, *i.e.* a contracted set of 35 functions based on a primitive set of 47 functions. The (*cc*-pVTZ) basis set for the H atom is constructed according to the contraction $(5s, 2p, 1d) \rightarrow [3s, 2p, 1d]$, *i.e.* a contracted set of 15 functions based on a primitive set of 17 functions. The *cc*-pVTZ molecular basis set for the C_6H_4 system contains $36s$, $26p$, $16d$, $6f$ contracted functions, a total of 236 contracted functions, constructed from a $80s$, $38p$, $16d$, $6f$ primitive set, a total of 316 primitive functions. The symmetry adapted basis functions in the *cc*-pVTZ molecular basis set for the C_6H_4 system divide between the irreducible representations of the C_{2v} group as follows: $80a_1$ $80b_1$ $38b_2$ $38a_2$

The "quadruple zeta" (*cc*-pVQZ) basis set for the C atom is a $(12s, 6p, 3d, 2f, 1g)$ set of primitive Gaussian-type function which is contracted to give a $[5s, 4p, 3d, 2f, 1g]$ set. The corresponding basis set for the H atom is constructed according to the contraction $(6s, 3p, 2d, 1f) \rightarrow [4s, 3p, 2d, 1f]$. The *cc*-pVQZ molecular basis set for the C_6H_4 system contains $46s$, $36p$, $26d$, $20f$, $6g$ contracted functions, a total of 450 contracted functions, constructed from a $96s$, $48p$, $26d$, $16f$, $6g$ primitive set, a total of 536 primitive functions. The symmetry adapted basis functions in the *cc*-pVQZ molecular basis set for the C_6H_4 system divide between the irreducible representations of the C_{2v} group as follows: $145a_1$ $145b_1$ $80b_2$ $80a_2$.

The correlation consistent basis sets described above form a systematic sequence of basis sets and therefore not only can the convergence of the various calculated energies be monitored with respect to basis set but extrapolation models can be invoked to afford estimates of the complete basis set limit.

3.2 Algorithms and Quantum Chemistry programs

All Brillouin-Wigner calculations reported in this work were performed by using the MOLCAS package of Karlström *et al* [5] together with computer code written to carry out the calculations based on the Brillouin-Wigner formalism.

Some calculations were repeated by using the GAUSSIAN package of Frisch *et al* [4]. Both MOLCAS and GAUSSIAN packages were used to carry out the matrix Hartree-Fock calculations and the *MP2* (*MBPT2*) calculations.

In the calculations using the MOLCAS package, molecular integrals over contracted Gaussian basis sets were evaluated by the SEWARD program by Lindh *et al* [84]. A conventional self-consistent field algorithm was employed with the threshold for changes in the energy set at 0.5×10^{-9}, the threshold for the

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density matrix and for the Fock matrix at 0.5×10^{-6}, and that for linear dependence at 0.1×10^{-5}. DIIS[4] extrapolation of the self-consistent field procedure was employed with a threshold of 0.15.

Optimal bond lengths and bond angles were taken from the work of Puiggros *et al* [76]. These authors optimized the geometries of the reactant, the transition state and the product. Dihedral angles were re-optimized in the present study.

4 Results

4.1 Calculated energies for a sequence of basis sets

The calculated energetics of the Bergman reaction supported by the correlation consistent basis set labelled *cc*-pVDZ are summarized in Table 1. In this table, E_{mHF} denotes the matrix Hartree-Fock energy and E_{MBPT2} is the standard second-order many-body perturbation theory energy, *i.e. MP2*. Values of E_{mHF} and E_{MBPT2} are given for the reactant, the transition state and the product. For each species total energies obtained by executing the MOLCAS package are given together with the corresponding values resulting from use of the GAUSSIAN program in [...].

In the column headed E_{MBPT2}, the third entry given for each of the species studied is the second order many-body perturbation theory estimate of the correlation energy obtained from the MOLCAS package. The energies obtained by employing the Brillouin-Wigner formalism are reported in the last two columns of Table 1 were calculated by using a computer code added to the MOLCAS program. $E_{\mathrm{MR\text{-}BWPT2}}$ denotes the energy corresponding to a multireference Brillouin-Wigner second order perturbation theory expansion. Introduction of the *a posteriori* modification described in section 2.2 leads to the energy values labelled by $E_{\mathrm{MR\text{-}MBBWPT2}}$, *i.e.* the multireference, many-body Brillouin-Wigner second order perturbation theory energy. The second entry for each species under these headings is the corresponding correlation energy estimate.

The last two rows of Table 1 show the calculated activation energy and reaction energy for each of the theoretical models employed. Again for the matrix Hartree-Fock and MBPT2 models, values derived from both the MOLCAS program and, in [...], from the GAUSSIAN package are presented.

The energies supported by the "triple zeta" correlation consistent *cc*-pVTZ basis set are displayed in Table 2 following the same conventions as those used in Table 1.

Table 3 presents the corresponding results for the largest basis set considered in this work, the "quadruple zeta" correlation consistent *cc*-pVQZ basis set. Again, we follow conventions used in Table 1.

[4] Direct Inversion of the Iterative Subspace extrapolation which was introduced by Pulay [85].

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Table 1
The energetics of the Bergman reaction determined from calculations using a "double-zeta" correlation consistent *cc*-pVDZ basis set. See text for full details.†

	E_{mHF}	E_{MBPT2}	$E_{\mathrm{MR\text{-}BWPT2}}$	$E_{\mathrm{MR\text{-}MBBWPT2}}$
Reactant	-229.396 595 43 [-229.396 595 40]	-230.191 305 63 [-230.191 305 70] -0.794 710 20	-230.038 072 88 -0.641 477 45	-230.191 607 43 -0.795 012 00
Transition state	-229.296 306 70 [-229.296 306 70]	-230.163 306 85 [-230.163 306 90] -0.867 000 15	-229.977 805 46 -0.681 498 75	-230.158 125 17 -0.861 818 47
Product	-229.277 831 55 [-229.277 831 60]	-230.213 177 01 [-230.213 177 00] -0.935 345 47	-230.004 245 11 -0.726 413 56	-230.186 249 20 -0.908 417 65
Activation energy	0.100 288 73 [0.100 288 70]	0.027 998 78 [0.027 998 80]	0.060 267 43	0.033 482 26
Reaction energy	0.118 763 88 [0.118 763 80]	-0.021 871 38 [-0.021 871 30]	0.033 827 77	0.005 358 23

† All energies are in Hartree atomic units.

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Table 2
The energetics of the Bergman reaction determined from calculations using a "triple-zeta" correlation consistent *cc-pVTZ* basis set. See text for full details.†

	E_{mHF}	E_{MBPT2}	$E_{\mathrm{MR\text{-}BWPT2}}$	$E_{\mathrm{MR\text{-}MBBWPT2}}$
Reactant	-229.455 783 57 [-229.455 783 50]	-230.466 296 11 [-230.466 296 10] -1.010 512 54	-230.262 853 89 -0.807 070 32	-230.466 326 80 -1.010 543 23
Transition state	-229.350 565 98 [-229.350 565 90]	-230.432 683 26 [-230.432 683 30] -1.082 117 28	-230.193 498 99 -0.842 933 01	-230.427 007 27 -1.076 441 29
Product	-229.330 108 09 [-229.330 108 20]	-230.479 769 51 [-230.479 769 50] -1.149 661 42	-230.216 669 22 -0.886 561 13	-230.451 256 84 -1.121 148 75
Activation energy	0.105 217 59 [0.105 217 60]	0.033 612 85 [0.033 612 80]	0.069 354 90	0.039 319 53
Reaction energy	0.125 675 48 [0.125 675 30]	-0.013 473 40 [-0.013 473 40]	0.046 184 67	0.015 069 96

† All energies are in Hartree atomic units.

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Table 3
The energetics of the Bergman reaction determined from calculations using a "quadruple-zeta" correlation consistent *cc-pVQZ* basis set. See text for full details.†

	E_{mHF}	E_{MBPT2}	$E_{\mathrm{MR\text{-}BWPT2}}$	$E_{\mathrm{MR\text{-}MBBWPT2}}$
Reactant	-229.469 911 73 [-229.469 911 70]	-230.613 696 46 [-230.613 696 40] -1.143 784 73	-230.383 269 68 -0.913 357 95	-230.613 652 11 -1.143 740 38
Transition state	-229.364 707 47 [-229.364 707 50]	-230.580 340 45 [-230.580 340 50] -1.215 632 98	-230.312 470 09 -0.947 762 61	-230.574 731 35 -1.210 023 87
Product	-229.344 449 42 [-229.344 449 56]	-230.626 724 96 [-230.626 725 00] -1.282 275 54	-230.335 222 62 -0.990 773 20	-230.598 204 68 -1.253 755 26
Activation energy	0.105 204 26 [0.105 204 20]	0.033 356 01 [0.033 355 90]	0.070 799 59	0.038 920 77
Reaction energy	0.125 462 31 [0.125 462 14]	-0.013 028 50 [-0.013 028 60]	0.048 047 06	0.015 447 44

† All energies are in Hartree atomic units.

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Two advantages arise from the use of sequences of basis sets, such as the correlation consistent sets: *a)* the ability to monitor the convergence of calculated expectation values with respect to basis set size; *b)* the possibility of extrapolation to the complete basis set limit. Extrapolation introduces an empirical element into the calculation.

In this work, we employ two different extrapolation procedures: *i)* the Hartree extrapolation formula, *ii)* an exponential extrapolation for the matrix Hartree-Fock energy combined with an inverse power extrapolation for the correlation energy.

The Hartree extrapolation formula [86, 87]

$$E(\infty) = \frac{E(2)\,E(4) - [E(3)]^2}{E(2) - 2E(3) + E(4)} \tag{55}$$

is based on three successive energies, $E(2)$, $E(3)$ and $E(4)$, for a given theoretical model. Equation (55) rests on the assumption that

$$E(n+1) - E(\infty) = m\,(E(n) - E(\infty)) \tag{56}$$

Equation(55) is obtained by writing down (56) for the cases $n = 2$ and $n = 3$, and then eliminating m. The Hartree extrapolation was employed by Ruedenberg and his coworkers [88], [89] for extrapolating energies supported by systematic sequences of basis sets to the complete basis set limit (for a recent review see [2]). The Hartree extrapolation has been used in other quantum chemical applications, for example, by Roothaan and Bagus [90] in extrapolating atomic self-consistent field calculations. We note in passing that the extrapolation formula suggested by Martin and Taylor [91] for use with sequences of correlation consistent basis sets

$$E(n) = E(\infty) + AB^{-n} \tag{57}$$

requires at least three points and, in the case of three points, is fully equivalent to the Hartree extrapolation (55).

Applying (55) to the matrix Hartree-Fock energies for the reactant given in Table 1, 2 and 3 for the *cc*-pVDZ, *cc*-pVTDZ and *cc*-pVQZ basis sets, respectively, −229.396 595 43 H, −229.455 783 57 H and −229.469 911 73 H, gives an extrapolated energy, $E(\infty)$, of −229.474 341 49H, some 4.430 mH below the energy corresponding to the *cc*-pVQZ basis sets. Application of the Hartree extrapolation to the matrix Hartree-Fock energies for the transition state and the product leads to the energies −229.369 692 33 H and −229.349; 871; 13 H, respectively, lying 4.985 mH and 5.422 mH below the corresponding energies supported by the *cc*-pVQZ basis sets.

When we turn our attention to the extrapolation of the energies which include an estimate of the correlation energy, there are two ways of proceedings. We can *(i)* carry out the extrapolation using the total energies supported by each of the three basis sets considered, so, for example, using the values of E_{MBPT2} for the reactant, −230.191 305 63 H, −230.466; 296; 11 H and −230.613; 696; 46 H, we can extrapolate using Hartree's formula giving −230.783; 982; 85 H; or

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(ii) perform the extrapolation for the correlation energies, −0.794 710 20 H, −1.010 512 54 H and −1.143 784 73 H, giving a correlation energy estimate of −1.358 996 71 H and then add the extrapolated correlation energy estimate to the extrapolated matrix Hartree-Fock energy, −229.474 341 49 H, yielding a total energy of −230.833 338 2 H, which is some 49.355 mH below the energy resulting from procedure *(i)*.

Table 4 collects the energies obtained by extrapolation to the complete basis set limit of the energies recorded in Tables 1, 2 and 3. For each method which takes account of electron correlation, two results are given corresponding to procedures *(i)* and *(ii)* defined above.

For the energy differences, *i.e.* the activation energy and the reaction energy, separate calculations can be carried out for the total energies obtained by procedures *(i)* and *(ii)*. A third possibility, which we label *(iii)*, is to extrapolate the energy differences supported by the three correlation consistent basis sets themselves. For example the matrix Hartree-Fock model yields activation energies of 0.100 288 73 H, 0.105 217 59 H and 0.105 204 26 H, respectively, from the *cc*-pVDZ, *cc*-pVTZ, *cc*-pVQZ basis sets. Extrapolation based on these three values gives an activation energy of 0.105 204 30 H.

The Hartree extrapolation formula is applicable to any series whether it is convergent, divergent or oscillatory. It could be described as purely numerical since it does not incorporate any information about the asymptotic behaviour of the series. The rate of convergence is determined by the ability of a finite linear combination of basis functions to duplicate any singularities in the exact wave function. The representation of the electron-nucleus and electron-electron cusps therefore affect the rates of convergence of atomic and molecular calculations. (For further discussion, see, for example, Schwartz [92], Klahn and Morgan [93, 94] and others[5]).

In a paper published in 1986, Klopper and Kutzelnigg [96] examined the nuclear cusp in the H atom and the convergence of linear combinations of Gaussian-type functions which they found to behave as $\sim \exp(-bN)$, where b is a constant and N is the number of s-type basis functions. For correlation consistent basis set *cc*-pVXZ, Feller [97,98] has suggested that a sequence of matrix Hartree-Fock energies can be extrapolated by a three parameter exponential model defined by

$$E_{\mathrm{SCF}} = a + b \exp\left(-cX\right) \tag{58}$$

in which a, b and c are to be determined by fitting to a sequence of calculations. In Table 4, energy values obtained by applying the extrapolation formula (58) are given in the row labelled *(a)*. The activation energy and reaction energy are determined from the extrapolated total energy values.

It is known that the correlation energy of the ground state of the He atom converges as $(\ell+1)^{-3}$. This was established in the work of Schwartz [92], of Carroll *et al.* [99], and of Kutzelnigg and Morgan [100, 101]. The exponential model (58) is therefore not suitable for extrapolation of the correlation energies. In the correlation consistent basis sets, functions of differing angular momentum

[5]For a recent review see [95].

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are added simultaneously if they yield a similar energy lowering. Helgaker *et al.* [102] proposed the two parameter form

$$E_{\text{correlation}} = a + bX^{-3} \tag{59}$$

for the extrapolation of correlation energies, where a and b are parameters to be determined by fitting, and X defines the *cc*-pVXZ basis set. Correlation energy values obtained by using the extrapolation (59) are given in Table 4 in the rows labelled *(b)*. Total energies obtained by adding the extrapolated matrix Hartree-Fock energies given by (58) to the extrapolated correlation energies given by (59) are also given in the row labelled *(b)*. Again, the activation energy and reaction energy are determined from the extrapolated total energy values.

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Table 4
The estimated complete basis set limit of the energetics of the Bergman reaction based on extrapolation from calculations using the sequence of correlation consistent basis sets designated *cc*-pVDZ, *cc*-pVTZ, *cc*-pVQZ. See text for full details.†

		E_{mHF}	E_{MBPT2}	$E_{\mathrm{MR\text{-}BWPT2}}$	$E_{\mathrm{MR\text{-}MBBWPT2}}$
Reactant	*(i)*	-229.474 341 49	-230.783 982 85	-230.522 204 47	-230.784 027 02
	(ii)		-1.358 996 71	-1.103 848 02	-1.359 222 07
			-230.833 338 2	-230.578 189 51	-230.833 563 56
	(a)	-229.474 325 62			
	(b)		-1.153 497 62	-0.919 623 66	-1.153 413 75
			-230.627 823 24	-230.393 949 28	-230.627 739 37
Transition state	*(i)*	-229.369 692 33	-230.759 462 91	-230.458 807 61	-230.754 846 58
	(ii)		-1.434 090 45	-1.14190297	-1.430 214 62
			-230.803 782 78	-230.51159530	-230.799 906 95
	(a)	-229.369 667 00			
	(b)		-1.225 118 23	-0.953 513 50	-1.219 377 04
			-230.594 785 23	-230.323 180 50	-230.589 044 04
Product	*(i)*	-229.349 871 13	-230.807 236 80	-230.484 948 85	-230.781 109 17
	(ii)		-1.497 527 82	-1.184 928 13	-1.473 219 54
			-230.847 398 95	-230.534 799 27	-230.823 090 67
	(a)	-229.349 839 29			
	(b)		-1.291 844 78	-0.996 413 94	-1.262 966 58
			-230.641 684 07	-230.346 253 23	-230.612 805 87
Activation energy	*(i)*	0.104 649 16	0.024 519 94	0.063 396 86	0.029 180 44
	(ii)		0.029 555 42	0.066 594 20	0.033 656 61
	(iii)	0.105 204 30	0.033 367 25	0.071 072 67	0.038 946 27
	(a)	0.104 658 62			
	(b)		0.033 038 00	0.070 768 78	0.038 695 34
Reaction energy	*(i)*	0.124 470 36	-0.023 253 95	0.037 255 62	0.002 917 85
	(ii)		-0.014 060 75	0.043 390 24	0.010 472 89
	(iii)	0.125 468 69	-0.013 003 61	0.048 377 56	0.015 462 70
	(a)	0.124 486 33			
	(b)		-0.013 860 83	0.047 696 05	0.014 933 51

† All energies are in Hartree atomic units.

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5 Discussion and Conclusions

In Table 5, we compare the estimates of the activation enthalpy and reaction enthalpy for the Bergman reaction determined in the present study using four methods:-

1. HF - (matrix) Hartree-Fock
2. MBPT2 - second order many-body perturbation theory
3. BWPT2 - second order Brillouin-Wigner perturbation theory
4. MBBWPT2 - second order many-body Brillouin-Wigner perturbation theory

with previous work and with laboratory experiment values.

The present study employed a sequence of correlation consistent basis sets. In particular, the correlation consistent basis sets *cc*-pVDZ, *cc*-pVTZ and *cc*-pVQZ were employed and from these an estimate of the complete basis set limit for each method was obtained by applying extrapolation procedures. We used two extrapolation procedures:- the Hartree extrapolation and an exponential formula for the matrix Hartree-Fock energy combined with an inverse power formula for the correlation energy.

Inspection of the calculated activation enthalpy and reaction enthalpy supported by the three basis sets and the corresponding extrapolated energy differences suggests that convergence with respect to basis set has been achieved. The activation enthalpy and reaction enthalpy supported by the *cc*-pVQZ basis set and the extrapolated values labelled *(iii)*, *(a)* or *(b)* differ by less than 0.6 kcal/mol.

Examination of the extrapolated values of the activation enthalpy based on the procedure labelled *(iii)* reveals that the value given by the Hartree-Fock model, 66.0 kcal/mol decreases to 20.9 kcal/mol when electron correlation effects are described by second order many-body perturbation theory, to 44.6 kcal/mol when second order Brillouin-Wigner theory is used, and 24.4 kcal/mol when the many-body variant of second order Brillouin-Wigner perturbation theory is employed. The activation enthalpy determined from laboratory studies is 28.7 kcal/mol. The laboratory value of the reaction enthalpy is 8.5 kcal/mol, which should be compared with the Hartree-Fock value of 78.7 kcal/mol, the *MBPT2* value of -8.2 kcal/mol, the *BWPT2* result of 30.3 kcal/mol, and the many-body *BWPT2* value of 9.7 kcal/mol. For both the activation enthalpy and the reaction enthalpy, the many-body, multireference Brillouin-Wigner perturbation theory taken through second order yields values which are closer to the laboratory value than either the *MBPT2* or *BWPT2* methods. Second order, many-body, multireference Brillouin-Wigner perturbation theory gives an activation enthalpy which differs by 4.3 kcal/mol from the laboratory value and a reaction enthalpy for which the corresponding difference is 1.2 kcal/mol.

The previous work compared with the present study in Table 5 employed the following theoretical methods:-

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1. CCSD - coupled cluster theory with single and double replacements
2. CCSD(T) - CCSD with perturbative estimate of the triple replacement component of the correlation energy
3. BD-CC(T) - Brueckner Doubles coupled cluster theory with perturbative estimate of the triple replacement component of the correlation energy
4. MR-BWCCSD - multi-reference Brillouin-Wigner coupled cluster theory with single and double replacements
5. MR-CI - multi-reference configuration interaction

The CCSD values of the activation and reaction enthalpies deviate significantly from the experimental values and this theory cannot provide a quantitative account for the ring-closure energy of the enediyenes. For the largest basis set employed in the CCSD calculations recorded in Table 5 (*cc*-pVTZ), the activation enthalpy differs by 9.5 kcal/mol from the laboratory value whilst for the reaction enthalpy the corresponding difference is 19.0 kcal/mol. The inclusion of a perturbative estimate of the correlation energy component associated with triple replacements in the theory designated CCSD(T) provides a quantitative description of the autoaromatization of hex-3-ene-1,5-diyne. For the *cc*-pVTZ basis set, the activation enthalpy supported by the CCSD(T) method differs from the laboratory value by 1.1 kcal/mol and the reaction enthalpy differs by 1.6 kcal/mol. For the multireference Brillouin-Wigner coupled cluster method MR-BWCCSD, the activation enthalpy differs from the laboratory value by 4.0 kcal/mol and the reaction enthalpy differs by 4.4 kcal/mol, again using the *cc*-pVTZ basis set. Finally, for the multireference configuration interaction results recorded in Table 5 for the *cc*-pVTZ basis set, the activation enthalpy differs from the laboratory value by 0.7 kcal/mol and the reaction enthalpy differs by 1.8 kcal/mol.

Second order, many-body, multireference Brillouin-Wigner perturbation theory is a robust and efficient approach to the electron correlation problem for systems requiring a multireference formulation. It is robust because the 'intruder' state problem associated with most other approaches to electron correlation using a multireference formalism is completely avoided. It is more efficient than alternative approaches and can be applied therefore *(i)* using larger basis sets thereby supporting higher accuracy; *(ii)* to larger (more extended) molecular systems. It can be systematically refined either *(a)* by taking the perturbation series to higher order or by summing certain classes of diagrammatic components through infinite order; *(b)* by refining the reference function.

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Table 5
Comparision of the estimates of the activation enthalpy and reaction enthalpy for the Bergman reaction determined in the present study with previous work and with laboratory experiment values. See text for full details.

Method	Basis set/ Extrapolation	Activation enthalpy $\Delta^{\neq}_{298}$ †	Reaction enthalpy Δ^{0}_{298} †
Laboratory[a]		28.7 ± 0.5	8.5 ± 1
Present work			
HF	*cc*-pVDZ	62.9	74.5
	cc-pVTZ	66.0	78.8
	cc-pVQZ	66.0	78.7
	(i)	65.6	78.1
	(iii)	66.0	78.7
	(a)	65.6	78.1
MBPT2	*cc*-pVDZ	17.6	-13.7
	cc-pVTZ	21.1	-8.4
	cc-pVQZ	20.9	-8.2
	(i)	15.4	-14.6
	(ii)	18.5	-8.8
	(iii)	20.9	-8.2
	(b)	20.7	-8.7
BWPT2	*cc*-pVDZ	37.8	21.2
	cc-pVTZ	43.5	29.0
	cc-pVQZ	44.4	30.3
	(i)	39.8	23.4
	(ii)	41.8	27.2
	(iii)	44.6	30.3
	(b)	44.4	29.9
MBBWPT2	*cc*-pVDZ	21.0	3.4
	cc-pVTZ	24.7	9.5
	cc-pVQZ	24.4	9.7
	(i)	18.3	1.8
	(ii)	21.1	6.6
	(iii)	24.4	9.7
	(b)	24.3	9.4
Previous work			
CCSD[b]	$6-31G^{**}$	37.1	26.2
	cc-pVDZ	35.4	25.7
	cc-pVTZ	38.2	27.5
CCSD(T)[b]	$6-31G^{**}$	27.0	5.1
	cc-pVDZ	26.4	4.4
	cc-pVTZ	27.6	10.1
BD-CC(T)[b,c]	*cc*-pVDZ	25.6	7.0
MR-BWCCSD[b]	$6-31G^{**}$	31.8	8.7
	cc-pVDZ	30.2	8.1
	cc-pVTZ	32.7	12.9
MR-CI[b,c]	$6-31G^{**}$	28.4	3.7
	cc-pVDZ	30.1	6.3
	cc-pVTZ	29.4	10.3

† in kcal/mol

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[a] Taken from the work of Roth, Hopf and Horn [56]. [b] Taken from the work of Puiggros *et al.* [76]. [c] This value includes a temperature correction [68]. [d] This value includes a Davidson-*like* correction.

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