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Phase factors in electron-molecule collision calculations

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Abstract

At low impact energies, high quality electron-molecule collision calculations require target correlated wavefunctions representing several electronic states. Target correlation is usually introduced via a configuration interaction (CI) expansion. This approach introduces phase factors in coefficients of the target CI expansion between the N electron target calculation and the $N+1$ electron scattering calculation. A method requiring rediagonalisation of the target calculation for each scattering symmetry was used (Orel et al., Phys Rev A 44 (1991) 4328) and widely copied. It is suggested that while this method accounts for the most serious phase problems, for certain calculations residual phase inconsistencies can arise. It is shown that the phase factors actually arise from different ordering of spin-orbitals in the N and $N+1$ electron calculations. An alternative method based on the analysis of the electron configurations used in the scattering calculation is proposed. This method resolves all phase ambiguities and removes the need for redundant rediagonalisations of the target Hamiltonian. The price of this method is the need to understand in detail the algorithm used for generating antisymmetrised configurations. Implementation of this method as part of the UK molecular R-matrix codes which are based on the ALCHEMY package is discussed.

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1. Introduction

Electron-molecule scattering calculations have grown rapidly in sophistication in recent years, as can be seen in the recent book on the topic edited by Huo and Gianturco [1]. For high quality calculations, and particularly ones considering electron impact electronic excitation, it is necessary to use correlated wavefunctions to represent the molecular target. The standard method of including this target correlation is via a configuration interaction (CI) expansion.

As first explicitly recognised by Orel et al. [2], and detailed below, the use of target CI expansions in scattering calculations can have problems with the signs of CI coefficients arising from the target and scattering calculations. A number of early R-matrix calculations [3,4] did not allow for these phase factors, giving rise to spurious results in some cases [5,6]. These problems are most likely to arise in high symmetry systems such as homonuclear diatomics and effect electronic excitation calculations. Thus, for example, calculations on electron scattering off N_2 found a signif-

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icant reduction in the X $^1\Sigma_g^+ \rightarrow$ B $^3\Pi_g$ cross section with inclusion of the correct phases [5]. Similarly, electron–O_2 calculations gave unphysical results when the phase corrections were neglected [6]. In contrast, for electron–H_2 scattering, the effect of phase correction was found to be only minor [7].

It is suggested that the method, referred to as the dummy orbital method below, used by Orel et al. [2] and adopted in recent R-matrix procedures [5,8,9], while removing the most serious phase problems, can still lead to undesirable phase inconsistencies in certain cases. An alternative method of performing phase corrected calculations, based on the ordering of spin orbitals, is proposed. This method not only removes all phase ambiguities but is computationally more efficient than the dummy orbital method. Furthermore, its relative simplicity means that one can predict analytically what phase factors, if any, will arise.

2. The dummy orbital method

In most ab initio electron–molecule collision calculations [1], the electronic wavefunction for an electron colliding with an N electron target is written as

$$\psi_k^\Gamma = \sum_{ijn} A\phi_{in}(x_1 \ldots x_N) u_{ij}^\gamma(x_{N+1}) a_{injk} + \sum_\ell \chi_\ell(x_1 \ldots x_{N+1}) b_{\ell k}, \qquad (1)$$

where A is the antisymmetrization operator and x_p represents the space-spin coordinates of the pth electron. The $u_{ij}(x)$ are orbitals representing the electron in the continuum. ϕ_{in} are target wavefunctions, defined in detail below, of symmetry Γ_i and index n within each symmetry.

In (1) the total wavefunction, ψ_k, has been given a symmetry label Γ. Similarly, the continuum orbitals have been labelled by their symmetry γ. γ is determined by the symmetry of the associated target state and the symmetry of the total wavefunction such that $\Gamma_i \otimes \gamma = \Gamma$. When both Γ_i and Γ are spatially degenerate, γ can take on more than one value. Thus, for example, the target state of state of a homonuclear diatomic such as H_2 of symmetry $^1\Pi_u$ can couple to the continuum orbital of both σ_u and δ_u to give functions of total symmetry $^2\Pi_g$.

The χ_ℓ in (1) are two-centre quadratically integrable, or L^2, functions introduced to relax orthogonality constraints imposed on the u_{ij} continuum orbitals, as well as, in some calculations, to account for polarisation effects not allowed for in the expansion over target states. As electronic states of the target are not projected from the χ_ℓ, these configurations do not give rise to phase factors. They will not be considered further.

If electron correlation effects in the target wavefunction in (1) are represented by a CI expansion, then

$$\phi_{in} = \sum_m c_{imn}\eta_{im}(x_1 \cdots x_N), \qquad (2)$$

where $\eta_{im}(x_1 \cdots x_N)$ represents a configuration of the N electron target. Phase problems arise because the sign of the individual target coefficients of the target CI expansion, c_{imn}, obtained explicitly when generating the target wavefunction, ϕ_{in}, and implicitly when generating the scattering wavefunction, ψ_k, may differ.

The dummy orbital solution to this problem implemented by Orel et al. [2] and others [5,8,9] is to generate the target wavefunction using the expansion

$$\phi_{in}^{\Gamma,\gamma} = \sum_m c_{imn}^{\Gamma,\gamma} A\eta_{im}(x_1 \ldots x_N) u_{ij}^\gamma(x_{N+1}), \qquad (3)$$

where a single, dummy, continuum orbital, of the appropriate symmetry, is used when generating the configurations which make up the target wavefunction. The extra electron must be antisymmetrised to each target configuration; it is used to enforce coupling to the symmetry, Γ, of the total scattering wavefunction of interest. A target state of the correct energy is generated by setting all integrals involving the dummy continuum orbital, u_{ij}^γ, to zero. Thus, for an H_2 target state of $^1\Pi_u$ symmetry, a dummy π_u orbital is used to enforce the required phases for a scattering calculation of $^2\Sigma_g^+$ symmetry, and separate calculations with dummy orbitals of σ_u and δ_u symmetry are required for a calculation of $^2\Pi_g$ overall symmetry.

The coefficients, $c_{imn}^{\Gamma,\gamma}$, obtained from this dummy orbital procedure have the same absolute value as those, c_{imn}, obtained by standard methods, defined by Eq. (2). However, besides overall sign ambiguities which are the result of any matrix diagonalisation, inspection of the coefficients reveal that there are symmetry-dependent sign changes between different coefficients.

The dummy orbital method has a number of advantages. In particular it can be implemented with little knowledge of the details of the method used to solve the CI problem or the exact cause of the phase changes. Furthermore, target configurations are automatically generated in the order required for constructing wavefunction (1).

However, the dummy orbital method requires rediagonalisation of the target Hamiltonians for each (Γ, γ) combination. As new procedures, such as [9], allow increasingly large target CI expansions, such repetition will become undesirable. Even more serious is the possibility that this procedure does not in fact cure all the phase consistency problems.

In general, wavefunctions are arbitrary to an overall sign. However, this sign should be consistent throughout a particular calculation. Thus, for example, the R-matrix method [10] divides configuration space into an internal region, where wavefunctions of form (1) are generated, and an external region where the coupling induced by the incident electron between various electronic states of the target is via off-diagonal (transition) moments of the target. In general these transition moments have an arbitrary sign. However, it is clear that the (explicit) sign of a moment in the external region should be the same as the (implicit) sign of that moment in the internal region. The dummy orbital procedure does not impose this condition.

There is a second, method independent, situation where the overall phase of the target wavefunction would appear to be significant. As mentioned above, in cases where the overall scattering symmetry and the target wavefunction are both spatially degenerate, the target state will couple to continuum orbitals of more than one symmetry. In the dummy orbital method, this means that two sets of target coefficients are required which may differ in their overall sign. Indeed, it will be shown below that, for a commonly arising case, the dummy orbital method ensures phase inconsistency.

3. The spin-orbital method

To resolve the various difficulties with the dummy orbital method, a new procedure has been developed. This method is based on the observation that the phase factors arise directly from the requirement of the configuration generation and symbolic matrix element construction procedures that the spin-orbitals used to construct Slater determinants for each configuration must arise in a standard, 'dictionary' [11] order. Although the requirement that spin-orbitals are occupied in a set order is general, the actual order required varies between different programs.

It should be noted that the dictionary ordering is required to define a phase convention but it is not usual to insist that Slater determinants are constructed using orbitals in this order. This is because other orderings may be more efficient for the much more time consuming steps of applying Slater's rules and evaluating matrix elements, see Bauschlicher and Lengsfield [12], for example.

The ALCHEMY configuration generator [13,14] utilized in the UK R-matrix suite [8] employs the convention that orbitals are ordered by symmetry and index. Thus for a $D_{\infty h}$ molecule, such as H_2, the orbital ordering is $1\sigma_g, 2\sigma_g, \ldots, 1\sigma_u, 2\sigma_u, \ldots, 1\pi_u, 2\pi_u, \ldots, 1\pi_g, 2\pi_g, \ldots$ and so forth. In practice the orbitals are ordered and numbered as spin orbitals. For degenerate orbitals, ordering is first on projection, λ, of the orbital and then on electron spin. The ALCHEMY ordering convention will assumed below.

Within this convention the phase differences arise because, as in Eq. (1), one wishes to work with $N+1$ electron configurations written $\phi_{in}(x_1 \ldots x_N) \times u_{ij}^{\gamma}(x_{N+1})$. However, the requirement on ordering of spin-orbitals may mean that this configuration needs to be reordered. This is seen most easily via an explicit example.

Consider an electron colliding with a molecular hydrogen target of ${}^1\Pi_u$ symmetry. Two typical target configurations might be $1\sigma_g 1\pi_u$ and $1\sigma_u 1\pi_g$. If the total symmetry of the scattering state, Γ, is ${}^2\Sigma_g^+$, the continuum orbital symmetry, γ, is π_u. In the ordering of Eq. (1), the appropriate $N+1$ electron configurations are $1\sigma_g 1\pi_u j\pi_u$ and $1\sigma_u 1\pi_g j\pi_u$, respectively. The first of these configurations is already in the correct spin-orbital ordering. The second needs to be rewritten as $1\sigma_u j\pi_u 1\pi_g$, where the interchange of two rows of the Slater determinant leads to a sign change.

This analysis clearly shows the source of the phase problem. A new procedure has been developed to correct for this problem. This procedure is based on the analysis of configurations such as those given in (3), which are in any case generated as part of any scattering calculation. For each target configuration the number, $N_{im\Gamma\gamma}$, of spin-orbitals occupied by target electrons arising *after* the dummy (prototype [9]) continuum orbital is identified. The target coefficients generated by the standard procedure (2) are then multiplied by a phase vector given by $(-1)^{N_{im\Gamma\gamma}}$, i.e.

$$c_{imn}^{\Gamma,\gamma} = (-1)^{N_{im\Gamma\gamma}} c_{imn} . \qquad (4)$$

For simple targets, such as the H_2 example used above and below, there are no further spin factors to consider. However, for many electron targets within the ALCHEMY codes there are three other sources of possible phase factors which can differ between N and $N+1$ electron calculations and therefore also have to be considered. These will be briefly sketched below.

The first factor arises from the method used to store configurations. For each calculation a reference configuration is defined. All configurations are then given in terms of a list of substitutions from this reference configuration. Each new configuration is generated by directly inserting replacement spin orbitals into the position in the list of vacated spin orbitals. This leads to configuration lists which are not necessarily in the dictionary order defined above and hence phase factors which may differ between the N and $N+1$ electron calculations.

The second source of phase factors arises from the need to adapt the configurations to both spatial and spin symmetry [15]. This leads to linear combinations of Slater determinants whose coefficients can differ in sign between the N and $N+1$ electron calculations.

The final phase factor arises only in the case where the overall scattering symmetry and target symmetry are both degenerate. As already mentioned, in this case it is necessary to consider coupling to continua of two separate symmetries. In the symmetry adaption discussed above, one component of the degenerate state is always used: for linear molecules this is the component with positive projection of the orbital angular momentum along the molecular axis, λ. For the continuum orbitals with lower λ value, the $N+1$ electron calculation couples the positive λ component of both the target and total symmetry. However, coupling to the continuum orbital with the higher λ value goes via a target projection with *negative* λ. This means that while all the configurations in the two cases have the same orbital occupancy, they differ by the occupation of one or more spin-orbitals. For all dummy orbital calculations tested, the N-electron target wavefunctions have the same phase factors for both components. The target phase factors generated for the lower component have therefore been assumed for the higher one.

4. Discussion

The spin orbital method only requires the generation of a single set of target CI vectors. This eliminates both the need for repeated target calculations and the possibility that phase inconsistencies can arise from the use of vectors which represent a single target state but are calculated by different means.

For simple cases, it is possible to use the spin-orbital method to evaluate phase corrections analytically. Thus, for example, one can consider the case where continuum orbitals of different symmetry are coupled to a single target state such as the H_2 $^1\Pi_u$ target state and $^2\Pi_g$ total symmetry case discussed above. Again consider the two typical target configurations $1\sigma_g 1\pi_u$ and $1\sigma_u 1\pi_g$. When the continuum orbital has σ_u symmetry the phase vector has the value $(-1,-1)$, conversely the δ_u symmetry orbital gives a phase vector $(+1,+1)$, i.e. the two possible couplings give rise to precisely the opposite phases. Although there is no general relationship between the phase vectors for the dual continuum case, analysis of a number of commonly occurring situation shows that the case of opposite phases is a fairly frequent occurrence.

With the ALCHEMY spin-orbital ordering convention, a special case arises for calculations comprising targets with two active electrons and states whose spatial symmetry is totally symmetric, i.e. Γ_i equals Σ_g^+, Σ^+ or A_1 for all i. In this case symmetry constraints ensure that electrons are always moved between orbitals of different symmetries in pairs[3], this means that for these systems the phase vector is always unity. Examples of such calculations are, ironically, the 3-coupled state electron - HeH^+ calculations of Orel et al. [2] for which the dummy orbital method was originally introduced, and similar calculations by Sarpal et al. [16].

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[3] It is possible to construct schemes where 3 or more electron movements can still couple back to the totally symmetric representation, but this violates the two active electron criterion.

In conclusion, a method of phase correcting the coefficients of target state configuration (CI) expansions has been developed. This method tackles this phase problem at the spin-orbital level thus removing the need to perform repeated diagonalisation of the target Hamiltonian. At the same time it corrects ambiguities in the overall phase of the wavefunction which can be significant in certain cases. The method has been implemented as part of the ALCHEMY based UK R-matrix program suite. However, implementation using other configuration generation algorithms will require knowledge of the spin-orbital ordering convention, the order in which the specific algorithm generates configurations for both target and scattering calculations, and any other internal factors which give rise to (potential) phase factors.

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