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Spin-dependent operators in the multi-shell approach to molecular quantum chemistry

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The aim of this thesis is to derive the matrix-elements of the spin-dependent $U(2n)$ generators in a multi-shell spin-orbit basis that is, a spin adapted composite Gelfand-Paldus basis. The advantages of such a multi-shell formalism are well known and well documented [**1**, **3**, **4**, **5**].

The approach taken exploits the properties of the $U(n)$ adjoint tensor operator Δ_{ij} ($1 \leqslant i, j \leqslant n$) as defined by Gould and Paldus in [**6**]. Δ is a polynomial of degree two in the $U(n)$ matrix $E = [E_{ij}]$. The unique properties of this operator allow the construction of adjoint coupling coefficients for the zero-shift components of the $U(2n)$ generators. The Racah factorization lemma may then be applied to obtain the matrix elements of all the $U(2n)$ generators.

This work is developed as follows. Chapter 1 reviews the basic concepts of the unitary group approach to quantum chemistry beginning with the second quantised form of the model Hamiltonian, H. H is expressible in terms of the generators of the unitary group $U(n)$, for spin-independence, and in terms of the $U(2n)$ generators for spin-dependence. This leads naturally to a need to evaluate the matrix elements of the $U(n)$ and $U(2n)$ generators in an appropriate basis. In our work we need to consider the Gelfand-Tsetlin (that is, the Gelfand-Paldus) basis and the spin-orbit basis together with their multi-shell extensions. After a general discussion of the state labelling problem for arbitrary irreducible representations of $U(n)$ we introduce the Gelfand-Paldus notation. This is obtained from an approach based on symmetry adaptation to the canonical subgroup chain. A generalization leads to the definition of the multi-shell spin orbit basis which is ultimately required in Chapter 8.

As an illustration of the basic concepts discussed in Chapter 1 we examine in Chapter 2 a molecular system with a three-shell partitioning of the model Hilbert space into core, active and external orbitals. Here we consider some aspects of complete active space configuration interaction calculations where excitations from the core are taken

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into account. For such a system it is appropriate to work in a basis for an irreducible representation of $U(n)$ which is symmetry adapted to the subgroup $U(n_0) \times U(n_1) \times U(n_2)$. Here n_0, n_1 and n_2 are the number of core, active and external orbitals respectively and $n_0 + n_1 + n_2 = n$.

We demonstrate that such a partitioning has the following advantages:

(i) It allows the efficient isolation of single, double and higher excitations from the reference space.

(ii) It explicitly demonstrates the internal-external factorization of generator matrix elements.

(iii) It allows the determination of the matrix elements of arbitrary products by simple matrix multiplications.

In Chapter 3 we outline the formalism of vector and tensor operators. This chapter constitutes the theoretical foundation of our approach. The behaviour of the $U(n)$ generators as a vector or contragredient vector operator and of the $U(2n)$ generators as an adjoint tensor operator allows their decomposition into shift components. In turn these shift components determine the action of a generator on a Gelfand-Paldus state. We also outline the Wigner-Eckart theorem and illustrate its use for the particular case of a vector-operator.

Chapter 4 begins with a review of the work of Gould and Paldus [**6**] and Gould and Battle [**2**] which evaluates the matrix elements of the del-operator in a Gelfand-Paldus basis. We then discuss the behaviour of the del-operator as an adjoint tensor operator together with its unique vanishing property on certain states. This latter fact leads directly to the definition of the zero shift adjoint coupling coefficient as the normalized del-operator matrix element.

We then demonstrate in Chapter 5 that this definition of the zero-shift adjoint coupling coefficients together with the use of the Racah factorization lemma enables us to obtain the Gould-Battle formulae for the del-operator matrix elements in a Gelfand-Paldus basis. Our approach is much simpler and yields more directly the basic segmentation level formulae.

In the following sections we generalize the ideas of Chapters 4 and 5 which were developed there for the Gelfand-Paldus or one-shell system. We do this first for the two-shell case and then for the general multi-shell case. The two-shell adjoint reduced Wigner coefficients are needed for the multi-shell work so they must be obtained first. It is organizationally convenient to look at the zero-shift case separately and we do this in Chapter 6.

The two-shell zero-shift adjoint coupling coefficients are proportional to the two-shell del-operator matrix elements. We first define the corresponding zero-shift adjoint reduced Wigner coefficients and then develop the Racah factorization lemma for the two-shell case. Evaluation of the reduced Wigner coefficients enables us to write down the two-shell del-operator matrix elements as a product of a reduced Wigner coefficients and an adjoint Wigner coefficient. The work of Chapter 6 may be applied to charge and spin densities in a two-shell system and this is briefly discussed.

In Chapter 7 we use the methods of Gould and his co-workers to evaluate the non-zero shift adjoint reduced Wigner coefficients, the non-zero shift adjoint coupling coefficients then follow immediately. Now, having obtained all the adjoint reduced Wigner coefficients we may write down the $U(2n)$ generator matrix elements in a two-shell spin-orbit basis using as a starting point the two-shell generalization of the formula of Gould and Paldus in [**6**].

Finally in Chapter 8, using the multi-shell formalism of Gould and Paldus [**3**] we make the final generalization and obtain the $U(2n)$ generator matrix elements in a multi-shell spin-orbit basis.

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