Symbolic Program for Generating the Many-body Perturbation-theory Formulas

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Abstract

The second quantized form of Rayleigh-Schrödinger perturbation theory is symbolically manipulated to derive many-body perturbation theory (MBPT) formulas for particle-hole excited states of closed-shell atoms. The analytic results obtained from the symbolic code, written in Mathematica [7], are presented for energies up to third order in MBPT. These results compare exactly with the results obtained by hand through third order [1]. We give, for the closed-shell atoms, analytic formulas for energies in first, second, and third order using the Hartree-Fock (HF) model. Numerical values for these energies can then be computed by using MathLink to call FORTRAN functions for the calculation of the two-electron integrals.

1 INTRODUCTION

Recent interest in the problem of predicting the effect of parity nonconservation in many-electron atoms at the 1% level [4, 6] has focused attention on the general problem of calculating many-electron atomic properties, such as energies and matrix elements, with high precision. A powerful approach, called MBPT, provides a systematic method for the calculation of atomic properties. However, calculational difficulties of each order of MBPT increases quickly, and therefore complete calculations of the atomic properties beyond third order in atomic physics have rarely been carried out. It is always of great interest to evaluate MBPT through the highest possible order. Once one
goes beyond first order, a large number of terms are generated and the problem of using MBPT quickly goes out of control.

We notice that in deriving higher-order corrections to the energy or matrix elements, there are generally two methods which may be used. The first method is the direct algebraic manipulation of creation and annihilation operators when the operators are converted into second quantized form. The second method is to make use of Goldstone diagrammatic techniques for expressing the results of perturbation theory. The advantage of the algebraic approach is that it is extremely straightforward, being essentially a direct application of the Wick’s theorem. A disadvantage of the diagrammatic approach is that it is possible to miss diagrams with complicated topology, and also that rules for symmetry factors require a great deal of experience to apply in high order. However, the second quantized algebraic approach is fairly straightforward to manipulate symbolically on conventional computers. Furthermore, our program automatically generates the terms which are translated and illustrated as the appropriate Feynman diagrams, thereby providing an easy check on the program integrity. For this purpose we have used the computer algebra system Mathematica to program Wick’s theorem. Mathematica provides several important features important for our purpose, e.g. it has built-in links to externally running programs, such as a FORTRAN or C program, via Mathlink. Another important feature of Mathematica is that it can handle algebraic or symbolic calculations through its list structure which is especially useful for the MBPT evaluations. Our main interest is the determination of the role that symbolic computation can play, when combined with existing numerical programs, toward solving a contemporary scientific problem.

In this paper, we show results for first-, second-, and third-order energies from the computer algebra system Mathematica. We have created explicitly the first- and second-order corrections to excited states of closed-shell atoms or ions. Specifically, we concentrate on particle-hole excitations, in which an electron is removed from one of the closed shells, creating a hole, and excited into a valence orbital, creating a particle. Such states have a richer spectrum than the alkali metals previously considered [5, 2], and formulas are much more complex.

2 MBPT FORMALISM

For most atoms, an exact solution to the Schrödinger or Dirac equation is not attainable because of the complexity of the Coulomb interaction between the electrons. A reasonable zeroth-order approximation can be made in which each electron is assumed to move independently in a central potential $V_{HF}(r)$ that describes the effect of other electrons. The actual interactions can then be accounted for in perturbation theory by splitting the Hamiltonian into two parts $H = H_0 + V$, where

$$H_0 = \sum_{i=1}^{N} h(r_i) + \sum_{i=1}^{N} V_{HF}(r_i) ,$$

$$V = - \sum_{i=1}^{N} V_{HF}(r_i) + \sum_{i \neq j}^{N} \frac{e^2}{r_{ij}} ,$$

where for the nonrelativistic case

$$h(r_i) = -\frac{\hbar^2}{2m} \nabla^2 + V_{nuc}(r_i)$$

and for relativistic case

$$h(r_i) = e \vec{a} \cdot \vec{p} + \beta mc^2 + V_{nuc}(r_i) .$$
Now $H_0$ and $V$ can be expressed in second quantized form as

$$H_0 = \sum_i \epsilon_i a_i^\dagger a_i^{} ;$$

$$V = \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} a_i^\dagger a_j^\dagger a_k a_l^{} - \sum_{i,j} (V_{HF})_{ij} a_i^\dagger a_j^{} ,$$

where $g_{ijkl}$ are Coulomb matrix elements defined by

$$g_{ijkl} = \alpha \int \frac{d^3r d^3r' u_i^\dagger(r) u_j^\dagger(r') u_k(r) u_l(r')}{|\vec{r} - \vec{r}'|} .$$

The Hartree-Fock potential is defined in terms of the Coulomb matrix elements by

$$(V_{HF})_{ij} = \sum_c (g_{iec} - g_{cjc}) ,$$

where the sum over the $c$ is taken to run over the filled core orbitals of the ground state of a closed-shell system. We are interested in particle hole excitation, and we adopt the convention that sums over $c,d,e,f...$ will be only over core orbitals (including the hole orbital), sums over $m,n,r,s...$ will be only over excited orbitals (including the particle orbital), and sums over $i,j,k,l$ will be over all orbitals. The letters $a$ and $b$ will be used for hole orbitals while the letters $v$ and $w$ will be used for the particle orbitals.

We create a zeroth-order particle-hole wave function with total angular momentum $J \mathbf{M}$ as

$$|0_{ph}\rangle = F_{av} a_i^\dagger a_j^{} |0_C\rangle ,$$

where $F_{av}$ is the angular coupling coefficient, $|0_C\rangle$ is the closed-shell wave function and we use the notation $a_i = a_{n_i l_m m_a}$, where $n_i$, $l_m$, and $m_a$ are the principal, orbital angular momentum, and magnetic quantum numbers for the specific electron. The zeroth order energy can be worked out as

$$H_0 |0_{ph}\rangle = F_{av} \sum_i a_i^\dagger a_i^{} a_j^{} a_i^{} |0_C\rangle ,$$

which gives

$$E^{(0)} = \sum_c \epsilon_c + \epsilon_v - \epsilon_a$$

### 3 FIRST- AND SECOND-ORDER ENERGIES

We choose the Hartree-Fock potential as the model potential. The reason we choose the HF potential is because there are large number of terms that cancel out automatically in the perturbation formulas and because it represents a reasonable approximation to the exact solution.

In this choice of model potential approximation, the perturbation $V$ simplifies to a simple form that can be written in second quantized normal ordered form as

$$V = \frac{1}{2} \sum_{i,j,k,l} g_{ijkl} : a_i^\dagger a_j^\dagger a_k a_l^{} : - \frac{1}{2} \sum_{c,d,e,f} (g_{cde} - g_{ced}) : a_i^\dagger a_j^\dagger a_k a_l^{} :$$

To understand the action of $V$ on $|0_{ph}\rangle$, it should be noticed that terms in Normal order

$$: a_i^\dagger a_j^\dagger a_k a_l^{} :$$


with core creation operators vanish, as do terms with excited-state annihilation operators. The second quantized form of the perturbing potential and these rules are straightforward to automate. All of the formulas presented here for the first- and second-order energies have been evaluated by hand and have also been evaluated with the algebraic manipulation language Mathematica [7].

To evaluate the first- and second-order energies, we need to solve

\[ E^{(1)} = \langle 0_{ph} | V | 0_{ph} \rangle \]  

and

\[ E^{(2)} = \langle 0_{ph} | V | 1_{ph} \rangle , \]

where \(|1_{ph}\rangle\) is obtained from the MBPT equation

\[ |1_{ph}\rangle = (H_0 - E^{(0)})^{-1}(E^{(1)} - V)|0_{ph}\rangle . \]  

\[ 4 \quad \textbf{RESULTS} \]

First-, second-, and third-order energies formula presented here are obtained from the computer algebra system Mathematica. We are now in the process of using MathLink to call an externally running FORTRAN program, patterned after the GRASP code [3], which calculates the relevant two-electron integrals. This approach permits one to use the power of a computer algebra system for the generation of which terms to sum and an optimized and mature numerical program to evaluate those sums.

\[ \textbf{References} \]


