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Configuration interaction calculations of annihilation rates for positronic complexes of alkali hydrides

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ABSTRACT

Ab initio multireference single- and double-excitation configuration interaction (MRD-CI) wave functions have been employed to compute the annihilation rates (AR) of positronic molecular complexes of four alkali hydrides. The first step in these calculations is the evaluation of integrals of the two-particle Dirac delta function δ_{+-} over pairs of electronic and positronic basis functions. MRD-CI wave functions calculated with the same basis are then employed to obtain expectation values of the δ_{+-} operator (Z_{eff}), which in turn are proportional to the corresponding annihilation rates (AR) of the associated many-particle states. The importance of removing near-linear dependencies in the basis sets employed is stressed as well as the advisability of placing diffuse (small-exponent) functions in the basis only at the most electronegative center of the molecule. A tendency to underestimate the Z_{eff} values is noted because of the impracticality of including sufficiently high-l basis functions in the basis for general molecular systems. However, comparison with the relatively accurate values for the four-electron e^+LiH complex obtained by Quantum Monte-Carlo (QMC) and other methods indicates that the fractional error is nearly constant over a large range of internuclear distance, consistent with the expectation that missing correlation effects in the MRD-CI treatment are predominantly atomic in nature. A scaling procedure based on the asymptotic δ_{+-} value, which is the same for all four alkali hydrides, is then shown to produce good agreement with the QMC AR data for e^+LiH. The same procedure has been applied to the δ_{+-} values for the positronic complexes of the heavier alkali hydrides for which no other theoretical results are available. Trends in the variation of the AR results with bond distance are discussed.

1. Introduction

The calculation of potential energy surfaces and positron affinities (PA) for many-electron positron–molecule complexes has been an important goal for *ab initio* calculations in recent years. However, much of the information available for such systems from experimental studies [1,2] deals with their electron–positron annihilation rates (AR). To obtain the maximum benefit from such calculations, it is therefore quite desirable to employ the computed wave functions for each system to evaluate properties other than energy, especially the expectation values (also referred to as Z_{eff}) of the two-particle density operator δ_{+-} that are directly proportional to the AR values for positron-molecule complexes.

In recent work [3], a series of computer programs has been developed to compute the energies of such systems within the framework of a multireference single- and double-excitation configuration interaction (MRD-CI) treatment. Applications have been carried out for the series of alkali hydrides [3–5] as well as a number of alkali oxides [6,7]. This work has shown that accurate potential curves can be obtained at the conventional (molecular) CI level, but also that the amount of the correlation energy itself is underestimated by a significant margin at this level of treatment. This is primarily because of the impracticality of employing high-l spherical harmonics [8] in the atomic orbital (AO) basis in calculations of molecular wave functions and potentials. Calculations employing the Quantum Monte-Carlo (QMC) method [9], the explicitly correlated Gaussian (ECG) [10] and stochastic variational (SVM) [11] methods *for systems with a small number of electrons* have demonstrated their superiority in describing electron–positron correlation effects as compared to conventional configuration interaction (CI) [4] techniques in which such high-l functions are absent. The positron is always found to have a quite diffuse charge distribution by virtue of the relatively small value of its mass. This is the main reason why high-l basis functions are required to obtain high accuracy in such calculations [8], since without them it is impossible to obtain a quantitative description of the positron's charge distribution in the neighborhood of each atomic nucleus and its inner shells. However, there is strong evidence to indicate that the missing correlation effects are predominantly atomic in

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nature [3–7]. The primary success of the MRD-CI calculations is that, when calculating potential energy curves for positron-molecule complexes without such high-l basis functions, atomic-like correlation effects are underestimated by nearly the same amount over the entire range of bond distance considered. Thus, one need only find the appropriate proportionality factor for absolute values of the energy.

The Dirac delta function is of much shorter range than the potential energy and so it is obvious that the importance of correlation effects will be magnified when the same wave functions are employed to obtain expectation values for this operator. In this case as well, high-l basis functions are the ideal recipe for overcoming such deficiencies. However, since this measure is no less easily applied for the computation of δ_{+-} expectation values than it is for Coulomb interactions, it might be concluded that molecular CI calculations are of little quantitative value in estimating AR values for such positron complexes. This assessment turns out to be too pessimistic, as we shall demonstrate in the following discussion. One can make use of the systematic character of the positron–electron correlation effects, particularly their tendency to remain fairly constant over a wide range of bond length. There are additional problems that arise because of the relatively short-range nature of the δ_{+-} operator, however, that first need to be addressed before significant progress can be made. When this is done, the wider range of applicability of conventional molecular CI treatments relative to the other methods mentioned above can be put to good advantage. This includes a high degree of flexibility in the choice of what kinds of electronic states can be treated as well as the number of active electrons and complexity of systems that can be described to a suitably high level of approximation.

2. Description of the computational method

The first step in constructing a program to compute AR values within the framework of a multireference CI is to compute integrals for the two-particle density operator δ_{+-} for atomic orbital (AO) basis functions. An algorithm introduced by Chandra and Buenker [12,13] has been employed to compute such integrals for arbitrary combinations of Cartesian Gaussian functions of different l quantum numbers. Because of the nature of the delta function, the desired results are obtained by evaluating four-center overlap integrals analytically. The resulting matrix of integrals is then subjected to the same four-index transformation as is employed for the Coulomb operator in the MRD-CI program for calculating Hamiltonian matrices [14–16]. Two of the four functions are taken from the positronic orthonormal set of orbitals, while the other two are electronic functions in each case.

While the above procedure is straightforward to implement, it was nonetheless found that care must be taken in the choice of basis functions in its application. Because of the short-range nature of the δ_{+-} operator (scaling as r^{-3} with interparticle distance r rather than r^{-1} as in the case of the Coulomb interaction), near-linear dependencies in the AO basis set are much more critical than in conventional treatments involving only the non-relativistic electrostatic Hamiltonian. For this reason it was decided to first transform away the eigenvectors of the overlap matrix with near-zero eigenvalue before proceeding with the orbital optimization step (usually a self-consistent field calculation). In addition, the diffuse functions needed to represent the occupied positron orbital are always placed on a single center, specifically at the location of the hydrogen atomic center in the present applications for positronic complexes of the alkali hydride molecules. The H AO basis employed for each of the four systems, LiH, NaH, KH and RbH, consists of 22 primitive s-type functions with exponents ranging from 100.0 to 0.000025 in a roughly geometric series, 15 of p type (exponents in the 4.0–0.0001 range), four of d type (exponents of 2.95, 1.206, 0.493 and 0.156) and three of f type (exponents 2.506, 0.875 and 0.274).

Otherwise, the same AO basis set is employed for each of the alkali atoms as in the previous calculations [3,4] of their hydride-plus positron potential energy curves (PEC). The diffuse functions (with exponent less than 0.06) in the original basis sets for the alkali atoms have been discarded in the AR calculations, however. The resulting potential energy curves are not affected significantly by this change of basis. In particular, the functions that were removed because of the linear-dependence threshold proved to be unimportant for energy calculations. They do, however, have a large effect on the δ_{+-} expectation values at relatively small bond distances, often producing unphysical variations in this quantity with decreasing bond distance. The same holds true for comparisons of basis sets with diffuse functions located at two centers instead of just at the location of the H atom.

The theoretical treatment employed in the present study thus proceeds as follows. First, an MRD-CI calculation with the same reference configuration sets as in previous work [3,4] is carried out to obtain the system's wave function at a given bond distance. The δ_{+-} expectation value is then obtained with this wave function by performing a single iteration in the conventional diagonalization procedure [16–18]. The positron–electron Coulomb integrals in the total energy calculations are simply exchanged on a one-to-one basis for their delta function counterparts in this procedure. Calculations have been carried out for each of the above four positron–alkali hydride complexes and the results are considered in the following section.

3. Discussion of results

The e^+LiH complex is a convenient test case for the above procedure because relatively accurate AR values for this five-particle system have been previously computed for it as a function of LiH bond distance by several groups employing a variety of methods: Mella et al. (QMC [19]), Strasburger (ECG [10]) and Mitroy and Ryzhikh (SVM [11]). Two sets of MRD-CI calculations have been carried out for the ground state, one in which the 1s electrons of Li are kept in a frozen core (2e CI) and one in which all electrons are involved in the excitation process (4e CI). The variation of the δ_{+-} expectation value with LiH bond distance for both treatments is shown in Fig. 1. The two curves are quite similar in shape, with the results for the large 4e CI lying somewhat lower. Both curves have a minimum near $r = 2.8\ a_0$ and increase sharply toward smaller bond distances.

When these results are compared with the more accurate data obtained in the QMC calculations [19], it is found that they are generally lower by more than a factor of two. Such an underestimation is expected based on the previous experience with the corresponding potential curves mentioned above. The deficiencies in the treatment of positron–electron correlation in the MRD-CI calculations are also responsible for the low δ_{+-} values. For example, at the dissociation limit in which the positronium hydride PsH system is formed, a δ_{+-} value of 0.02056 a_0^3 is obtained for the 2e CI treatment and 0.0195 a_0^3 for the 4e CI. The corresponding QMC value [19] is 0.04794 a_0^3 (at $r = 20.0\ a_0$). The QMC data have the same general variation with bond distance, however, as would be expected if the correlation error in the MRD-CI calculations is atomic-like in nature, as has already been indicated in the potential energy calculations mentioned above [3,4].

If the raw data in Fig. 1 are scaled so as to have agreement with the QMC δ_{+-} expectation value at large r, the curves of Fig. 2 result. There is a much higher degree of consistency between all three sets of results when this scaling procedure is carried out (Table 1). The scaled 2e CI results agree better with the QMC data at large r values