Positron Binding Energies for Alkali Hydrides

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Received: February 8, 2005; In Final Form: May 2, 2005

Ab initio multireference single- and double-excitation configuration interaction (MRD-CI) calculations are carried out to study the interactions of positrons with the members of the alkali hydride class of molecules. A new computer program has been constructed for this purpose that makes use of the Table-Direct-CI method for construction of the required Hamiltonian matrixes and electronic/positronic wave functions. The calculations indicate that the binding energy (positron affinity PA) of a single positron to these systems increases by an increment of 0.2−0.3 eV as the atomic number of the alkali atom is increased. It is found that the positron prefers a location in the more electronegative regions of such molecules, similarly as has been found in earlier calculations for the urea and acetone molecules. The positron orbital itself possesses a diffuse charge distribution with relatively small expectation values of the kinetic energy in all four systems considered. Each of the four positronic molecules is stable with respect to formation of either positronium (Ps) or HPs according to the present calculations. Relatively large changes in the equilibrium bond distance of the hydrides occur as a result of the positron interaction. The importance of bond dipole moments in producing the binding of positrons to molecules is discussed, as well as the role that the electronegativity of the constituent atoms plays in determining the magnitude of the PA for a given system.

I. Introduction

It is well established that the positron and electron have almost all the same values for their physical constants. They differ in the sign of their electric charge, however, and this fact leads to many interesting distinctions in their chemical reactivity. It has been argued theoretically that a molecule with a dipole moment that is larger than a critical value of 1.625 D[1−3] can form an infinite number of bound states with either an electron or a positron. All alkali hydrides discussed in the present work fulfill this condition. The electron has been experimentally observed to form stable bound states with a large number of molecules (anions). A molecular field can trap the electron temporarily, thereby forming a resonant state that decays after a finite lifetime to various channels. For this reason, electron-attachment processes have attracted a great deal of interest in both basic and applied science. If such a decay channel couples strongly with a fragmentation channel, then the molecule can decompose and produce various kinds of products.[4] It has been speculated[5] that the positron may also form stable (bound) or metastable (resonant) states with molecules, producing positive molecular ions. It is well known, however, that, when a positron is in the same location as an electron, they undergo mutual annihilation by emitting two or three γ rays. Consequently, it appears possible that both positron-bound and -resonant states may decay either by annihilation or by positron escape after a finite lifetime. Recent measurements by Gilbert et al.[6] and Barnes et al.[7] have provided strong evidence for the formation of positronic bound or metastable states with alkanes, including a measure of their binding energy.

If positron binding really does occur, then the mechanism for forming a bound state (or attachment), as well as corresponding decay processes, should be grossly different for it than for an electron, and hence, the corresponding fragment products should also differ. It is the task of quantum mechanical calculations to explore these possibilities in an a priori manner.

Kurtz and Jordan were the first to carry out ab initio self-consistent field (SCF) calculations of positron affinities (PA) for molecules.[8] One of the most important results of their calculations is the diffuseness of the molecular orbital (MO) occupied by the positron. It was speculated on this basis that electron−positron correlation effects would be relatively unimportant. Nonetheless, earlier work by Clary[9] employing the configuration interaction (CI) Hylleraas method for the H^-/e^+

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10.1021/jp050687f CCC: $30.25

(H−positronium, HPs) system indicated that positron−electron correlations are more difficult to describe than those of the conventional electron−electron type. Bromley and Mitroy[10] later underscored this point in a quantitative manner in their configuration interaction calculations of PsH and Be/e^+. The same group[11] has recently given a review of progress in computing the PAs of atoms and the corresponding annihilation rates by a variety of techniques.

The most accurate calculations to date on positronic systems, albeit relatively few molecular studies, have been carried out with the stochastic variational method (SVM),[11−13] quantum Monte Carlo (QMC) methods,[14,15] and by employing explicitly correlated Gaussian (ECG) basis sets (also employed in the SVM treatment).[11,16,17]

Probably the best-studied molecule in this general field is lithium hydride LiH. It is the lightest of the alkali hydrides and therefore accessible to the most accurate computational methods available. Bubin and Adamowicz[16] obtained a PA value of 0.038312 hartree with the ECG technique, as compared to earlier results of 0.0333 hartree employing the diffusion Monte Carlo technique[15] and 0.0170 hartree with CI calculations.[18]

The objective of the present work is to carry out a systematic study of the PA values for the series of alkali hydrides from LiH to RbH employing recently developed CI programs based on the Table-Direct CI approach that has been widely used in electronic structure calculations.[19−21] The latter programs allow one to carry out multireference single- and double-excitation CI calculations (MRD-CI method) with the help of configuration selection techniques[20,22] and perturbative energy corrections. As noted by Bromley and Mitroy,[10] the main difficulty in applying the CI method to positron binding on molecules is the attractive electron−positron interaction. When it results in significant Ps-like electron−positron clusters, their representation by single-particle functions centered on the nuclei requires inclusion of high angular momentum quantum numbers.[10] In the case of positrons binding with atoms, positronium may be preferably formed and bind to the positive atomic ion if the ionization potential of the neutral atom is lower than the Ps binding energy (0.25 Hartree). In the case of positron binding with molecules, however, the energy balance for determining the boundary condition can also lead to the production of neutral fragments, i.e., dissociation of $M_1M_2e^+$ to $M_1^+ + M_2Ps$ (e.g., HPs in the present case of alkali hydrides) or $M_1M_2^+ + Ps$.

The systems of interest have a large number of electrons, and the accuracy requirements for the proposed calculations are relatively high. It was therefore decided that a new series of computer programs were needed for this purpose that go well beyond the Hartree−Fock (HF) level of treatment. Nonetheless, it is clear from the experience of other computational methods for atoms and small molecules discussed above that there are clear limitations on the accuracy that one can reasonably expect from CI calculations for such relatively large systems. Our earlier work on the effects of positron binding on the urea and acetone molecules[23,24] has shown that the HF method underestimates their PA values by a wide margin. A recent CI treatment of positronic formaldehyde[25] has also demonstrated this point quite clearly. The present CI treatment differs from that employed in ref 23 primarily in that it expands the class of electron−positron excitations that are considered explicitly in the final secular equations.

II. Brief Description of the Computational Method

The first step in any CI procedure is to calculate various types of integrals involving a basis of one-particle functions. It is clear that different functions are required for an optimal description of a positron charge distribution than for a system of many electrons contained in a molecule. In the previous calculations on urea and acetone,[23,24] we have simply employed a different, more diffuse, set of Gaussian-type atomic orbitals for the lone positron than for the electrons of the system. In the present work, a different approach has been taken, however, namely, to use the same set of functions for both the positron and the electrons. This approach allows one to compute electron-repulsion integrals involving each combination of basis functions without making any change to standard programs employed in conventional electronic structure calculations (the Hondo integral program[26] has been used in the present work). Kinetic energy integrals can also be treated in the same manner. Two sets of one-particle energy integrals need to be stored, however, which combine the nuclear attraction and kinetic energy contributions: the sum must be stored for electrons and the difference for positrons. The original MRD-CI program package[20,21] employs a symmetry transformation, that is, computes integrals over symmetry orbitals for Abelian groups. This program also can be taken over with only minor changes to describe electron−positron interactions (a separate transformation has to be carried out for each set of kinetic energy/nuclear attraction integrals because of the difference in sign of the electric charge of the two types of particles).

The resulting transformed integrals are then employed as input to an appropriately modified open-shell SCF program. The procedure in actual use is restricted to closed shells of electrons and a single open-shell positron, since the systems of primary interest all have this type of configuration. The Roothaan open-shell algorithm[27] has been modified for this purpose. Account has been taken of the opposite electric charges of the two types of particles and also of the absence of the exchange interaction between positrons and electrons. The resulting SCF-MOs are sorted according to the irreducible representations (IRs) of the appropriate Abelian group or subgroup in a given application (C_{2v} for the present applications). Note that at this stage there are *two* sets of MOs, each expanded in the same set of atomic orbitals, as discussed above.

The next step in the calculations is the four-index integral transformation over the above (orthonormal) one-particle functions. The corresponding one-particle transformations are carried out quite simply in each basis, using the appropriate kinetic energy/nuclear attraction integrals over atomic basis functions in each case. The electron−electron transformation is carried out without any modification to the existing MRD-CI routines. For the corresponding electron−positron transformations, twice as many additional integrals are needed. This is because one has a choice of whether to use the orthonormal *electronic* basis for the first particle or the second. Because the number and type of basis functions is the same for both the positron and the electrons, it is convenient to use the same indexing scheme to store the three types of integrals. The latter are all stored as electron-repulsion integrals (this procedure amounts to specifying a sign convention for these quantities). When the integrals are later retrieved in the various CI steps, it is necessary to determine which of the three classes of integrals is required in a given case. If a positron−electron interaction is involved, the sign of the stored integral is changed before using it to obtain the desired Hamiltonian matrix element. The possibility of employing a fixed core of electronic closed shells in the CI calculations is also provided for in the resulting integral transformation program, including the use of relativistic effective core potentials (RECPs).

The above preparations allow one to carry out a given CI treatment in much the same way as in conventional electronic structure calculations. In particular, the Table CI methodology[19] can be taken over with only minor changes in the original code. The most significant modification involves the handling of the four-index (electron-repulsion) integrals required when applying the Slater−Condon rules[28] in computing a given interaction between pairs of configurations. First of all, one must check whether all of the indices are for electronic basis functions or only two of them. The answer to this question determines which of the three categories of integrals is required in a given case (electron−electron repulsion, electron−positron attraction with the electron pair index being either greater or less than that of the positron pair index). The sign of the interaction is clearly affected by this relationship. Second, the exchange permutation is ignored in the case of a positron−electron interaction. Otherwise, the existing electronic structure code[20] can be taken over with only a small number of modifications. This is important since there are a large number of cases in which such four-index integrals are required.

The MRD-CI method[19−22] works exclusively with many-particle basis functions that are eigenvectors of the S^2 operator. It does not make any difference whether all the particles are electrons or one or more of them are positrons when forming linear combinations of Slater determinants that diagonalize S^2. For example, one electron and one positron in open shells lead to two states of singlet and triplet multiplicity. This is one of the main reasons why it is relatively easy to adapt the existing Table-CI[19,20] code to the present requirements. To distinguish positron orbitals from their electronic counterparts, the convention has been adopted of representing the positron orbitals by negative integers. The input for the CI program therefore consists of a number of reference configurations each denoted by a single negative index and an appropriate number of positive integers indicating the doubly and singly occupied electronic MOs in a given case. On this basis, all singly and doubly excited configurations with respect to the reference set are generated and the standard perturbative selection procedures[20,22] are carried out. The diagonalization of relatively large Hamiltonian matrixes is then accomplished with the aid of the Davidson method[29] (the current limit on the product of the order of the secular equation and the number of roots obtained is 2×10^7).

III. Results of the MRD-CI Calculations

A. Comparison with Benchmark Studies for LiH/e$^+$. The simplest alkali hydride system LiH has been the subject of a number of exhaustive computational studies of positron binding employing the quantum Monte Carlo (QMC)[15,30,31] and ECG methods.[16,32,33] It is evident that the type of conventional CI treatment described in the previous section is incapable of achieving the high level of accuracy attained in these previous studies. One nonetheless expects that CI will have a notably broader range of applicability than the QMC and ECG methods. The goal in the present work is therefore to carry out MRD-CI positron binding calculations at a feasibly high level of accuracy that is at least comparable throughout a series of molecules containing a fairly large number of electrons.

Specifically, this means employing atomic orbital (AO) basis sets with a maximum L value of 3 or 4 and restricting the CI space itself so as to fall well short of the AO basis limit (full CI). In their study of the PsH system, Bromley and Mitroy[10] have found that CI calculations with $L_{\max} = 3$ yield a total energy of −0.7750785 Hartree, for example, as compared to their SVM value of −0.7891961 Hartree. A MRD-CI calculation employing two f functions has been carried out with the present programs. It gives a variational ($T = 0$) energy of −0.771946 Hartree. Adding the MR-Davidson correction (FCI)[34−36] improves this result to −0.775082 Hartree, quite close to the limiting (variational) value for $L_{\max} = 3$ given above. On the other hand, it is comparatively easy to obtain high accuracy for H$^-$ itself, as well of course for Ps and the H atom. As a result, the above underestimation of the HPs total energy leads to relatively large percentage errors in positron binding energies. (HPs is bound by 0.025082 Hartree instead of by 0.039196 Hartree,[10] and the dissociation energy into H + Ps is only 63.99% of the exact value.) It is therefore clear that there is a strong tendency for CI calculations carried out with the type of AO basis sets common in present-day molecular calculations to produce PA values that are significantly smaller than their experimental counterparts. One has to balance this concern with another basis fact, however, namely, that there are no measured PA values to compare with, at least at the present time. It is therefore hoped that the information that is obtained from such calculations is sufficiently accurate to provide experimentalists with reliable information about the relative magnitudes of molecular PA values, particularly about trends that occur in a given class of systems such as the alkali hydrides in the present case.

The basis sets employed for the present LiH and LiH/e$^+$ MRD-CI calculations are taken from the EMSL Basis Set Library (http://www.emsl.pnl.gov/cgi-bin/ecce/basis_old.pl). In the case of hydrogen, the cc-pV5Z set has been used[37] (excluding the g function), while for lithium the cc-pV5Z basis of Feller has been taken. As noted in section II, several additional diffuse-type Gaussian functions (five of s-type with exponents 0.01, 0.005, 0.0025, 0.0010, and 0.0005, four of p-type with exponents 0.009, 0.006, 0.003, and 0.0009, and one d-type function with 0.056 exponent) have been added to each molecular basis to aid in the description of the positron charge distribution. In accordance with previous experience,[23,24] these functions are located at the most electronegative atom of a given system, which for the alkali hydrides is always the H atom. Tests have been made to study the effect of placing additional diffuse functions at the other nuclear center, and the resulting total energies have always been found to agree to within 0.02−0.05 eV of those obtained with only the hydrogen-centered diffuse functions for a given MH/e$^+$ system. Because of the increased difficulties in obtaining an orthogonal one-electron basis in the latter test calculations, it was decided to employ only the above H-centered set of diffuse functions in the final treatment. The resulting molecular AO basis has been employed for *both* the electrons, and the single positron of the system rather than using a separate basis for each type of particle.

The results obtained in the present study for the LiH molecule and the combined LiH/e$^+$ system are shown in Table 1. The SCF total energies for both systems agree quite closely with the earlier calculations of Strasburger.[18] The present LiH total energy is 0.0010 Hartree lower, while the corresponding LiH/e$^+$ values agree to better than 0.0001 Hartree. The present SCF LiH PA value is only 0.132 eV, as compared to the value of 0.149 eV obtained in earlier work.[38] Potential curves have been computed for each system and the equilibrium bond distances r_e obtained are 3.033 bohr for LiH and 3.10 bohr for LiH/e$^+$.

The MRD-CI results have been obtained without employing configuration selection ($T = 0$). The minimum LiH total energy in this treatment is −8.06591 Hartree (secular equation order is 4243) for $r_e = 3.019$ bohr (exptl value = 3.015 bohr). Applying the perturbational MR-Davidson correction (FCI in

TABLE 1: Computed Minimum Total Energies (E_T/Hartree) and Equilibrium Bond Distances (r_e/bohr) for the LiH and LiH/e$^+$ Systems Obtained in the Present Work at Various Levels of Theoretical Treatment and Comparison with Results of Other Authors[a]

	LiH		LiH/e$^+$		
treatment	E_T	r_e	E_T	r_e	PA
SCF	−7.987313	3.033	−7.992164	3.102	0.132
SCF[b]	−7.98628	(3.015)	−7.99211	(3.015)	(0.159)
SCF[c]				3.209	0.149
$T = 0$	−8.065907	3.019	−8.089984	3.324	0.657
FCI	−8.068266	3.019	−8.097643	3.324	0.800
$T = 0$ core	−8.02434	3.05	−8.05132	3.30	0.734
FCI core	−8.025432	3.045	−8.056746	3.391	0.852
CI[c]			−8.015646	3.327	
CI[b]	−8.03830	(3.015)	−8.05530	(3.015)	(0.463)
QMC[d]	−8.0704		−8.1037		0.907
QMC[e]	−8.0704	3.015	−8.1072	3.458	1.001
ECG[f]	−8.070449		−8.104850		0.936
ECG[g]	−8.070538[i]		−8.107474	3.348	1.005
ECG[h]	−8.066428	(3.061)	−8.104740	(3.445)	(1.042)

[a] The corresponding positron affinities (PA/eV) are also given [b] Reference 18, vertical results [c] References 24, 38. [d] Reference 15. [e] Reference 30. [f] Reference 32. [g] Reference 33. [h] Reference 16. [i] Reference 39.

Table 1) lowers the energy by 0.0024 Hartree without altering the r_e value significantly. The lowest total energy reported to date for this system is −8.070538 Hartree,[39] which is 0.002272 Hartree below the above FCI value.

The present MRD-CI total energy for the LiH/e$^+$ system is −8.089984 Hartree at the $T = 0$ level (secular equation order 163777) and −8.097643 Hartree at the FCI level. The computed r_e value is 3.324 bohr in each case. Strasburger[33] has reported a total energy of −8.107474 Hartree on the basis of ECG calculations. The corresponding r_e value is 3.348 bohr. Bubin and Adamowicz[16] have reported a non-Born−Oppenheimer LiH/e$^+$ total energy of −8.104740 Hartree, also by employing the ECG method. Mella et al.[30,31] have obtained a very similar minimum total energy of −8.1072(2) Hartree but a notably larger r_e value of 3.458 bohr, on the basis of their QMC treatment.

As expected, it is found that the deficiency in the present computed correlation energies is greater for the positronic system. This fact leads to an underestimation of the LiH PA value, 0.657 eV at the $T = 0$ level and 0.800 eV for the FCI level of treatment. The corresponding adiabatic PA values of refs 30 and 33 are 1.001 and 1.005 eV, respectively. The MR-Davidson correction[34,35] clearly leads to better agreement of the MRD-CI results with the most accurate LiH PA values obtained to date, since it has a significantly greater effect on the positronic system as on the neutral LiH molecule. The corresponding energy required for decomposition into Ps + LiH$^+$ is computed to be 1.675 eV, so the positronic molecule is stable with respect to this channel as well.

The balance in correlation energy for the two systems can be further improved by restricting the active space of electrons to exclude the 1s core of lithium. This procedure causes a greater increase in energy (0.043 Hartree) for LiH than for the positronic system (0.041 Hartree), thereby leading to an increase of the computed PA value to 0.852 eV. Since the electron−positron correlation energy is more difficult to describe,[11,13] increasing the number of active electrons in the CI tends to be *less* favorable for the positronic system. There is also a tendency to overestimate r_e values, however, when this is done (Table 1).

The overall conclusion that results from the above calculations is that, although MRD-CI calculations employing typically flexible AO basis sets for relatively large systems will inevitably lead to an underestimation in PA values, the discrepancies can be minimized by (a) applying the MR-Davidson correction[34,35] and (b) by using a frozen core of electrons in the definition of the CI spaces.

TABLE 2: Computed Minimum Total Energies (E_T/Hartree) and Equilibrium Bond Distances (r_e/bohr) for the NaH and NaH/e$^+$ Systems Obtained in the Present Work at Various Levels of Theoretical Treatment[a]

	aH		NaH/e+		
treatment	E_T	r_e	E_T	r_e	PA
SCF	−162.39163	3.60	−162.40249	3.80	0.296
SCF[b]				3.63	0.285
$T = 0$ core	−162.55859	3.58	−162.58882	3.97	0.823
FCI core	−162.56530	3.597	−162.60332	4.115	1.034

[a] The corresponding positron affinities (PA/eV) are also given. [b] Reference 38.

B. NaH/e$^+$. On the basis of the above experience with calculations for LiH and LiH/e$^+$, it was decided to employ a 1s^2 frozen core in the MRD-CI calculations for NaH and NaH/e$^+$. An uncontracted version of the cc-pVTz set given in the EMSL Library has been chosen to describe the sodium atom. The hydrogen atom basis[37] is the same as that employed in the LiH calculations. In addition, the same 5s4p1d set of primitive Gaussians has also been included at the H center to describe the relatively diffuse charge distribution of the positron. As noted in section II, all the basis functions are available for both the electrons and the single positron in the calculations.

The results obtained in the present study are shown in Table 2. The computed PA value for NaH at the SCF level of treatment is 0.296 eV. This value is 0.164 eV greater than that given in Table 1 for LiH. The present SCF PA value is 0.011 eV greater than in our previous study.[38] There is an increase in the equilibrium NaH bond distance of 0.20 bohr upon adding the positron according to the present SCF calculations.

The corresponding MRD-CI calculations have been carried out at zero threshold ($T = 0$). The secular equation order is 861025 for NaH/e$^+$, as compared to that for NaH itself of only 67959. These values are notably larger than for the fixed core treatment of the lithium hydride systems (163777 and 4243, respectively) because of the larger number of active electrons for NaH (10 vs 2). The PA value obtained at this level of treatment is 0.823 eV, 0.527 eV greater than in the SCF calculations. This increase is somewhat less than that found for the fixed-core LiH calculations (0.602 eV, Table 1).

The MR-Davidson correction[34,35] is 0.00671 Hartree for NaH, but it is 0.01450 Hartree for the positronic system. As a result the PA value increases to 1.034 eV after this adjustment is made to the total energies (FCI in Table 2). The increase relative to the $T = 0$ value is 0.211 eV. The corresponding increase for LiH is only 0.118 eV. As mentioned above, the MR-Davidson correction is expected to favor the positronic system because the correlation effects are more difficult to describe in this case than for the neutral molecule. The fact that the increase in the PA value relative to the $T = 0$ result is significantly greater for NaH than for LiH is consistent with this conclusion because of the greater number of active electrons in the MRD-CI treatment of the heavier system. The FCI PA value for NaH is 0.182 eV larger than for LiH. The latter result underestimates the best previously computed (Born−Oppenheimer) PA value[30,33] for LiH by 0.15 eV. On this basis, one can expect the exact PA value for NaH to be at least 1.18 eV, that is, 0.15 eV greater than the present FCI result (Table 2). No experimental value is as yet available for comparison. The discrepancy may in fact

TABLE 3: Computed Asymptotic Total Energies (E_T/Hartree) for the Alkali Hydride MH/e$^+$ Systems Obtained in the Present Work at the MR-Davidson Corrected (FCI) Level of Theoretical Treatment[a]

system	E_T	D_e	ΔE (Ps)
LiH/e$^+$	−8.055902	0.04175	0.06156
NaH/e$^+$ (core)	−162.57845	0.02487	0.04174
KH/e$^+$ (core)	−600.016725	0.01203	0.02662
RbH/e$^+$ (core)	−2939.123841	0.00798	0.02345

[a] The corresponding dissociation energies to M$^+$ + HPs (D_e/Hartree) and for formation of Ps + MH$^+$ (ΔE (Ps)/Hartree)) are also given.

be larger than 0.15 eV in this case because of the greater number of electrons in NaH. The energy required for Ps formation is 1.136 ev, 0.539 eV less than the corresponding quantity for LiH/e$^+$, reflecting the fact that the IPs of the alkali hydrides decrease with atomic number.

The computed NaH bond length is 3.597 bohr at the FCI level, as compared with the known experimental value of 3.57 bohr. As before with LiH, this value increases significantly upon addition of a positron. The r_e value in this case is 4.115 bohr (Table 2), an increase of 0.518 bohr. By contrast, the corresponding increase for the LiH system is only 0.305 bohr (Table 1). This difference can be attributed in large measure to the fact that NaH is more weakly bound than its lighter counterpart.

Another effect of the more weakly bonding characteristics of NaH shows up in the computed value for the dissociation energy of NaH/e$^+$ relative to Na$^+$ + HPs. The present value for this quantity is 0.02487 Hartree. This result may be compared to the corresponding value of 0.04175 Hartree for LiH (Table 3). The latter value is larger than the best Born−Oppenheimer results obtained to date (0.0382[30] and 0.036936 Hartree;[33] the nonadiabatic value obtained in ref 16 is 0.036548 Hartree). This dissociation process can be conveniently analyzed as occurring through the intermediate, Na + H/e$^+$, although this species is not computed directly as the dissociation product in the NaH/e$^+$ potential curves. The final HPs product then results by ionizing the alkali atom valence electron and attaching it to the H/e$^+$ system (which is not bound and thus possesses an energy of −0.5 Hartree) to form HPs. Since it is easier to both break the bond of the NaH/e$^+$ system and ionize an electron from the Na atom than is the case for the corresponding Li systems, it is clear that the overall production of HPs requires less energy in this case, as found in the present study. Of this amount, the difference in computed IPs accounts for 0.01385 Hartree (exptl value = 0.00930 Hartree), whereas the remaining part is due to the difference in bond energies of the NaH/e+ and LiH/e+ systems.

C. KH/e$^+$. The AO basis chosen for the potassium hydride calculations is of CVTZ type.[40,41] It is employed in uncontracted form and is augmented by the same set of diffuse functions as in the LiH and NaH calculations already discussed. The Ne core of 10 electrons is frozen in the MRD-CI treatment so that the number of active electrons is the same as for NaH. The motivation for this choice was to ensure the best possible balance in the treatment of correlation effects for these two systems. In addition, another set of MRD-CI calculations has been carried out with relativistic effective core potentials (RECP) for the K atom,[42] with the same number of active electrons (10) as above. This procedure clearly assumes that the core potentials should be equally applicable to both the valence electrons and the positron of the KH/e$^+$ system. This approach entails an element of pragmatism in that the core potentials include the exchange interaction which is important for valence electrons but is not operable for a positron. Especially since the positron orbitals are invariably found to be quite diffuse, it is felt that such an approximation is quantitatively justified. The main purpose of the RECPs in the present context is to provide an accurate representation of the electrostatic interaction of the shielded nuclei with the positron, and there is good reason to believe that this objective is suitably fulfilled by their use.

TABLE 4: Computed Minimum Total Energies (E_T/Hartree) and Equilibrium Bond Distances (r_e/Bohr) for the KH and KH/e$^+$ Systems Obtained in the Present Work at Various Levels of Theoretical Treatment[a]

	KH		KH/e$^+$		
treatment	E_T	r_e	E_T	r_e	PA
SCF	−599.69553	4.44	−599.71882	4.74	0.634
SCF RECP	−28.46442	4.40	−28.48754	4.75	0.629
SCF[b]				4.365	0.592
FCI no core	−600.069358	4.20	−600.116143	4.90	1.273
T = 0 core	−599.95900	4.25	−600.00042	4.87	1.127
FCI core	−599.97848	4.250	−600.02875	5.063	1.368
T = 0 RECP	−28.74070	4.24	−28.78143	4.85	1.108
FCI RECP	−28.76167	4.242	−28.81110	5.043	1.345

[a] The corresponding positron affinities (PA/eV) are also given. [b] Reference 38.

The SCF PA value obtained in the calculations without the RECP is 0.634 eV (Table 4). This result is 0.042 eV higher than that obtained in our earlier study.[38] The present value is 0.338 eV greater than obtained for NaH (Table 2). The MRD-CI calculations for both KH and KH/e$^+$ are carried out without configuration selection (T = 0). The orders of the corresponding secular equations are 99156 and 320343, respectively. The T = 0 PA value is found to be 1.127 eV, an increase over the SCF value of 0.493 eV.

The corresponding PA value after making the MR-Davidson correction is 1.368 eV (FCI in Table 4), an increase relative to the T = 0 result of 0.241 eV. The corresponding increase for NaH is 0.211 eV (Table 2), only slightly smaller. The computed NaH bond length in the parent system is 4.250 bohr, which compares favorably with the experimental value of 4.240 bohr. There is a sizable increase in this bond distance in the presence of the positron to a value of 5.063 bohr. The corresponding T = 0 value is only 4.87 bohr. This sensitivity to the effects of higher excitations is mainly due to the flatness of the KH/e$^+$ potential curve. The correction itself amounts to 0.02833 Hartree for KH/e$^+$ (at the potential minimum), as compared to only 0.01450 Hartree for the corresponding NaH energy difference. This distinction arises mainly from the respective c^2 values for the reference configurations in the final wave functions (ca 93% for NaH/e$^+$ and only 90.5% for KH/e$^+$).

The computed dissociation energy into K$^+$ + HPs is 0.01203 Hartree at the present level of treatment. This represents a decrease of 0.01284 Hartree relative to NaH (Table 3), and thus the expected trend discussed above toward smaller barriers to dissociation of the alkali hydrides with increasing atomic number is confirmed by this result. The computed decrease in ionization potential (IP) in going from Na to K is 0.02830 Hartree (5.013 eV vs 4.243 eV) is thus larger than the decrease in dissociation energy (experimental IP values are 5.139 and 4.341 eV, respectively). The energy required for Ps formation is only 0.724 eV, 0.412 eV less than for NaH/e$^+$. This value is thus smaller than the KH PA value but is still greater than the dissociation energy to HPs (0.327 eV).

The calculations with the K RECP give quite similar results as with the frozen electronic core obtained from the all-electron SCF calculations. The FCI PA value is 1.345 eV, only 0.023 eV less than before without employing the RECP. The computed

TABLE 5: Computed Minimum Total Energies (E_T/Hartree) and Equilibrium Bond Distances (r_e/bohr) for the RbH and RbH/e$^+$ Systems Obtained in the Present Work at Various Levels of Theoretical Treatment[a]

	bH		RbH/e$^+$		
treatment	E_T	r_e	E_T	r_e	PA
SCF	−2938.886490	4.65	−2938.914591	5.15	0.765
SCF[b]				4.773	0.824
$T = 0$ core	−2939.060728	4.45	−2939.111056	5.25	1.369
FCI core	−2939.071457	4.416	−2939.131822	5.481	1.643
$T = 0$ RECP	−24.498256	4.42	−24.547331	5.19	1.335
FCI RECP	−24.509833	4.412	−24.568660	5.402	1.601

[a] The corresponding positron affinities (PA/eV) are also given. [b] Reference 38.

bond lengths are 0.008 bohr (KH) and 0.020 bohr (KH/e$^+$) smaller when RECPs are used to represent the potassium core electrons. In each case the differences are too small to give a clear indication of the extent to which they are attributable to relativistic effects. The results at least show that there is no fundamental objection to employing the same RECP for positrons as for valence electrons.

D. RbH/e$^+$. The all-electron AO basis employed for the rubidium atom ($Z = 37$) has been optimized by one of the authors (MT[43]) in our previous study.[38] It consists of a 22s15p9d set and is employed in an uncontracted form. In addition, the same set of diffuse Gaussians is added to describe the positronic orbital as with the lighter alkali hydrides. The total energy results for both RbH and RbH/e$^+$ are given in Table 5. As before, all-electron SCF calculations are first carried out to generate the basis of orthonormal one-particle functions to be employed in the ensuing MRD-CI calculations. All the Rb shells except for 4s, 4p, and 5s are included in the frozen core in the CI treatment, leaving 10 active electrons for the RbH system, the same as for NaH and KH. Parallel calculations have been carried out with an RECP for the Rb atom[44] in which only 10 electrons are treated explicitly. The same all-electron basis is employed in these calculations as above to ensure an optimal comparison between the two sets of results (Table 5).

The PA value obtained at the all-electron SCF level of treatment is 0.765 eV. This result is 0.059 eV lower than in our previous study.[38] The difference is due to the fact that a separate AO basis has been employed for the positron as for the electrons in the earlier work. The additional diffuse functions have a notable effect on the electronic part of the wave functions, particularly for the neutral RbH system, thereby decreasing the PA value somewhat.

The MRD-CI calculations are again carried out without configuration selection ($T = 0$). The orders of the secular equations in the frozen core treatment are 102682 and 331744 for RbH and RbH/e$^+$, respectively. The $T = 0$ PA value increases to 1.369 eV as a result of including electron correlation at this level. The corresponding FCI value is 1.643 eV, which is 0.275 eV greater than for KH, somewhat smaller than the 0.334-eV increase computed in going from NaH to KH (see Tables 2 and 4). The size of the MR-Davidson correction is only 0.010729 Hartree for RbH and 0.020766 Hartree for the positronic system, again underscoring the relative importance of higher-order excitations for the description of electron−positron correlation. The energy required for Ps formation is 0.638 eV, while that for dissociation to HPs is only 0.217 eV, so the RbH/e$^+$ system is bound with respect to all three of the above channels.

The corresponding results with the Rb RECP[44] are also shown in Table 5. The bond distance values obtained in the two treatments are quite similar. For RbH the computed values are 4.416 bohr and 4.412 bohr, for example, as compared with the experimental value of 4.47 bohr. Addition of a positron increases the equilibrium bond length, as in the lighter systems. The corresponding values differ by a more significant amount in the case of the positronic system, 5.481 bohr in the frozen core calculation and only 5.402 bohr in that employing the RECP. The latter result is a manifestation of the fact that the RbH potential curve is notably flatter for the positronic molecule, causing the bond length to be more sensitive to changes in the description of the electronic core of the Rb atom. The PA value itself is 0.042 eV smaller when the RECP is employed. It is difficult to say what part of this rather small difference is due to relativistic effects, however, since the core description at the nonrelativistic level is also different in the two treatments.

IV. Positronic Charge Distributions

The wave functions obtained in the MRD-CI calculations discussed in the previous section have been employed to compute the charge distributions of the four MH/e$^+$ systems. The electronic distributions are shown in parts a−d of Figure 1, whereas the corresponding positronic distributions are shown in parts a−d of Figure 2. The results are obtained for the respective equilibrium MH bond distances in each case. In parts a−d of Figure 1, the region in the immediate neighborhood of the alkali atom's nucleus has been left blank for purposes of clarity. The ionic character of the various molecules is clear from these diagrams, particularly as one proceeds to the heavier systems. The steady increase in equilibrium bond length is also apparent. The decreasing trend in dissociation energies to M$^+$ + HPs is easily understandable on the basis of these diagrams.

The positron distributions in parts a−d of Figure 2 demonstrate that the main portion of the positronic density is centered behind the hydrogen atom in each case. There are always two maxima, a smaller one near the H nucleus itself and then a broader one about 2.0 bohr behind this point, on the opposite side of the metal atom. The density surrounding the latter atom shows a steadily decreasing trend as its atomic number increases. This is at least partially explained by the increase in bond length of the positronic system from LiH/e$^+$ to RbH/e$^+$

Our previous study of urea and acetone[23,24] has indicated that the positron charge density in those cases is centered on the oxygen atom in each case, that is, on the most electronegative atom in these systems. This result is consistent with the present results for the alkali hydrides, since the more electronegative atom for such systems is always the hydrogen. The positronic charge distribution is quite diffuse, however. This can be seen most easily from the MRD-CI $T = 0$ expectation value of the positron kinetic energy in each case. It has a value of only 0.0524 Hartree in LiH/e$^+$, about the same as for an $n = 3$ Rydberg AO of the H atom. Similar values are obtained for the heavier MH/e$^+$ systems (0.05257 Hartree for RbH/e$^+$). For comparison, the positron kinetic energy for urea has been calculated to be only 0.0150 Hartree. These results are consistent with the increasingly contracted nature of the positron density around the H atom in parts a−d of Figure 2. The corresponding nuclear repulsion energies for the positron are 0.5300 (LiH), 1.5657 (NaH), 2.5491 (KH), and 4.6644 (RbH) Hartree. The present data emphasize that the electronic shielding of the metallic nucleus is only partially complete, as is well known from electronic structure theory. The expectation value of the positron−electron Δ function is proportional to the 2γ annihilation rates of these systems,[11] and work is in progress to calculate these quantities. Qualitatively, it appears from the positronic density diagrams in parts a−d of Figure 2 that the annhilation

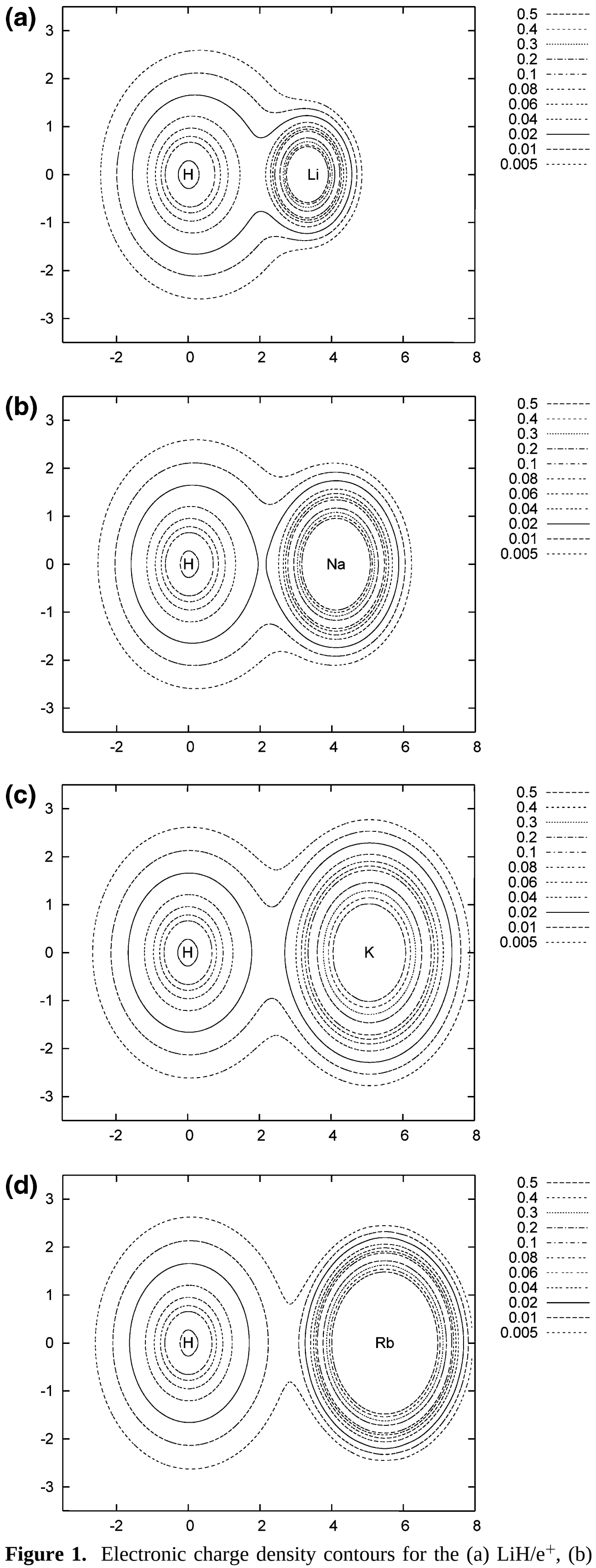

Figure 1. Electronic charge density contours for the (a) LiH/e$^+$, (b) NaH/e$^+$, (c) KH/e$^+$, and (d) RbH/e$^+$ systems computed in the present work.

rate should increase steadily as the atomic number of the metallic atoms increases.

The trends in the positronic and electronic charge distributions discussed above are consistent with the fact that the dipole moments of the alkali hydrides increase with atomic number of the heavy atom. The dipole moments for the neutral hydrides computed in the present study are shown in Table 6. They are generally smaller than obtained in our previous work[38] at the HF level of treatment, with the difference increasing with atomic number. The corresponding computed equilibrium bond lengths

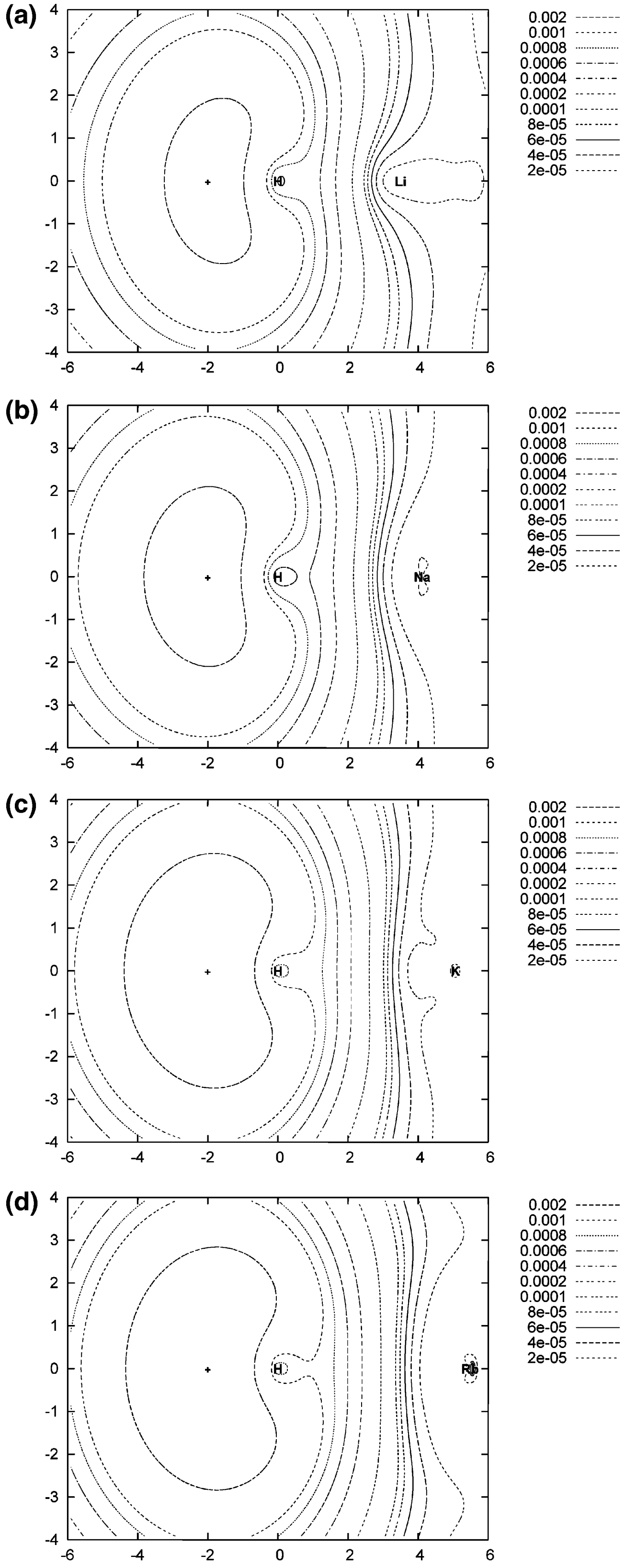

Figure 2. Positronic charge density contours for the (a) LiH/e$^+$, (b) NaH/e$^+$, (c) KH/e$^+$, and (d) RbH/e$^+$ systems computed in the present work.

TABLE 6: Computed Bond Distance r_e (bohr), Dipole Moment μ (au), and Positron Affinity PA (eV) at the FCI Level of Treatment (see text) for the Alkali Hydride Molecules

molecule	r_e	μ	PA
LiH	3.045	2.323	0.852
NaH	3.597	2.717	1.034
KH	4.250	3.393	1.368
RbH	4.416	3.551	1.643

TABLE 7: Comparison of the Computed Bond Distances (in bohr) of the Neutral Alkali Hydrides (MH) and the Corresponding Molecular Ions with Attached Positron (MH/e^+)[a]

molecule	r_e (MH)	r_e (MH/e+)	%
LiH	3.045	3.391	11.4
NaH	3.597	4.115	14.4
KH	4.250	5.063	19.1
RbH	4.416	5.481	24.1

[a] The percentage increase in each case is also indicated.

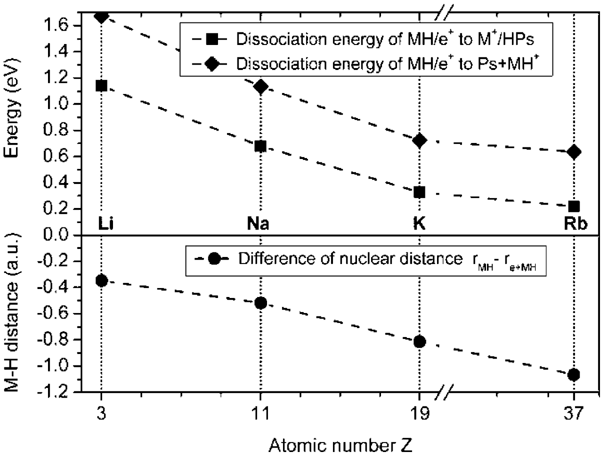

Figure 3. Trends in the dissociation energy of MH/e^+ to $M^+ + HPs$ and $Ps + MH^+$ and bond length difference between MH and MH/e^+.

are also given. There is a close correspondence between these two sets of values, with ratios of 1.311, 1.324, 1.252, and 1.243 bohr/au in the four cases, as one would expect for such ionic systems. This effect also explains in good measure why the HF dipole moment values are higher, because the corresponding r_e values are also larger when correlation effects are neglected.

The computed bond lengths are also interesting in another context. The percentage increase upon adding a positron increases rather strongly with the atomic number of the alkali atom (Table 7). It is twice as large for RbH as for LiH, for example. One possible explanation for this trend is that, for such a light atom as Li, the positron tends to form a bound state on the tail of a long-range polarization potential, therefore causing relatively little change in the bond distance. The heavier alkali atoms have increasingly lower electronegativities, however, and so the increased polarity of the chemical bond makes it progressively easier for the positron to attach itself to the electronic cloud in the neighborhood of the hydrogen atom (see parts b−d of Figure 2). The resulting trend toward formation of a closed-shell (H^-) electronic configuration within the molecular ion, i.e., nascent HPs, would therefore be expected to gradually weaken the bond with the metal atom, which is at least consistent with the results of Table 7. It will be interesting in future work to explore these relationships further, both by means of new calculations and also experimentally. The trends in bond length increase upon adding a positron and in $M^+ + HPs$ and $MH^+ + Ps$ dissociation energies are summarized in Figure 3.

Finally, as mentioned in the Isntroduction, there is a theoretical argument which indicates that a fixed dipole moment of at least 1.625 D = 0.640 au is sufficient to have bound positronic states, although there is also evidence from ab initio calculations[25] that such a threshold is too low. The present computed PA values for the alkali hydrides are also shown in Table 6 to consider this point. The ratios of PA to dipole moment (in eV/au) for the four molecules are fairly constant: 0.367 (LiH), 0.381 (NaH), 0.403 (KH), and 0.463 (RbH). This shows that there is a definite correlation between these two quantities and that the above ratio decreases rather slowly as the dipole moment is lowered. It also should be recalled that the present PA values are likely to be underestimated by at least 15% based on the benchmark studies for LiH/e^+. On this basis, it would be difficult to draw a clear conclusion about whether a minimum dipole moment value exists below which positron binding cannot occur, since the above ratios decrease so slowly from RbH to LiH while the positronic density in these systems varies rather strongly. Since the water molecule does not appear to have bound states with a positron,[25] despite its dipole moment of 1.8 D, there is a clear indication that the dipole moment threshold varies from one class of molecules to another. This is consistent with two facts, namely, that (1) the electric field of the molecule only coincides with that of a fixed dipole asymptotically and generally varies when a positron is added, and (2) the possibility of dipole-bound states does not exclude positron binding on the local electronic density or positronium formation within the range of the molecular system. There is at least another key factor, namely, the identity of the most electronegative atom in the system. In the latter case, it is oxygen, whereas for the alkali hydrides it is the hydrogen atom, for which the electronic density is far less compact. The relatively small PA values obtained in CI calculations for urea and acetone[23] and formaldehyde[25] are certainly consistent with this supposition.

V. Summary

A new configuration interaction package has been developed to calculate the energies and wave functions of molecular systems in the presence of a lone positron. The standard techniques of the MRD-CI method have been implemented for this purpose, including configuration selection and perturbative energy extrapolation. The same AO basis has been employed in each case for both the electrons and the positron, whereby the latter is found quite generally to prefer a relatively diffuse (Rydberg-like) charge distribution.

The present work has centered upon the alkali hydride systems, LiH, NaH, KH, and RbH, and their interaction with a positron. Very accurate results for the first of these systems are available from the ECG and QMC methods, and thus it was possible to gauge the effectiveness of the MRD-CI method in treating such problems by comparing with these data. The lowest variational ($T = 0$) result for the LiH/e^+ total energy obtained in the present study is 0.017 Hartree (0.46 eV) higher than the most accurate value available from the latter calculations. This discrepancy is reduced to 0.010 Hartree by applying the MR-Davidson correction (FCI result). The corresponding deficit in total energy for the LiH molecule itself is only 0.002 Hartree at ostensibly the same level of CI treatment, so it is clear that it is considerably more difficult to account for electron−positron correlation than is the case for electron pairs. One of the consequences of this situation is therefore that positron affinities are significantly underestimated in the MRD-CI calculations.

The present result for the LiH PA is 0.800 eV, as compared to the best available values in the literature of 1.001 and 1.005 eV. This discrepancy is reduced by employing the frozen core approximation, that is, by keeping the 1s shell of the Li atom doubly occupied in all configurations. This procedure favors the positronic system and thus increases the PA value by 0.052 eV so that the remaining discrepancy is 0.15 eV.

On the basis of these benchmark calculations, it was decided to treat the heavier alkali hydrides with a frozen core in each case, so that only 10 active electrons are employed in the MRD-CI calculations for all three systems. Calculations with RECPs have also been carried out with the same number of active electrons. The best (FCI) PA values obtained in these calculations increase steadily with the atomic number of the alkali atom: 1.034 eV for NaH, 1.368 eV for KH, and 1.643 eV for RbH. The bond length of each of these three systems increases significantly upon adding a positron. The difference relative to the corresponding neutral hydride molecule is computed to be 0.51 bohr for NaH, 0.81 bohr for KH, and 1.07 bohr for RbH. The steadily increasing trend in these quantities (the value for LiH is only 0.35 bohr) is seen to be primarily due to the increasing flatness in the MH/e^+ potential curves with atomic number of the alkali atom. Dissociation energies into the most stable products ($M^+ + HPs$) decrease fairly regularly as a result (0.04175 Hartree for LiH and only 0.00798 Hartree for RbH, for example).

Analysis of the computed wave functions shows that the positron assumes a more contracted charge distribution as the atomic number of the metal atom is increased. In all cases the positron density is centered near the H atom because of the latter's higher electronegativity. The kinetic energy of the positron is found to increase in going from Li to Rb, but the computed values are still indicative of a Rydberg-like charge distribution for each of the four molecules studied. There is a clear correlation between the dipole moment and PA values of these systems. The more ionic the molecule, the greater the equilibrium internuclear distance and, hence, the greater the dipole moment, which in turn allows the positron to attach itself more strongly to the electronic charge cloud in the neighborhood of the hydrogen atom.

Acknowledgment. The authors wish to thank the Deutsche Forschungsgemeinschaft for their support (Grant Bu 450/14-1) as well as the Verband der Chemischen Industrie (R.J.B., H.-P.L., and V.M.). The work was also supported in part by the Ministry of Education, Science, Sport, Culture and Technology, Japan Society for Promotion of Science for Japan-Germany Collaborative Research Project, Collaborative Research Grant from National Institute for Fusion Science and Yamaguchi University (L.P., M.T., and M.K.). L.P. also acknowledges partial support by a JSPS Grant-in-Aid for young scientists and Academic Frontier Research Program by MEXT.

References and Notes

(1) Fermi, E.; Teller, E. *Phys. Rev.* **1947**, *72*, 399.
(2) Turner, J. E. *Am. J. Phys.* **1977**, *45*, 758 1977.
(3) Garrett, W. R. *J. Chem. Phys.* **1980**, *73*, 5721.
(4) Christophorou, L. G. *Electron−Molecule interactions and their applications*; Academic Press: New York, 1985; Vols. 1 and 2.
(5) Moxon, J.; Shrader, D. M.; Laricchia, G.; Xu, L.; Hulett, L. D. *Phys. Rev. A* **2000**, *62*, 052708. Surko, C. M.; Passner, A.; Leventhal, M.; Wysocki, F. J. *Phys. Rev. Lett.* **1988**, *61*, 1831.
(6) Gilbert, S. J.; Barnes, L. D.; Sullivan, J. P.; Surko, C. M. *Phys. Rev. Lett.* **2002**, *88*, 043201. Sueoka, O.; Kawada, M. K.; Kimura, M. *Nucl. Instrum. Methods Phys. Res., Sect. B* **2000**, *171*, 96.
(7) Burnes, L. D.; Gilbert, S. J.; Surko, C. M. *Phys. Rev. A* **2003**, *67*, 032706; Surko, C. M.; Gribakin, G. F.; Buckman, S. J. *J. Phys. B: At. Mol. Opt. Phys.* **2005**, *38*, R57.
(8) Kurtz, H. A.; Jordan, K. D. *J. Chem. Phys.* **1981**, *75*, 4.
(9) Clary, D. C. *J. Phys. B* **1976**, *9*, 3115.
(10) Bromley, M. W. J.; Mitroy, J. *Phys. Rev. A* **2001**, *65*, 012505.
(11) Mitroy, J.; Bromley, M. W. J.; Ryzhikh, G. G. *J. Phys. B* **2002**, *35*, R81.
(12) Kukulin, V. I.; Krasnopolsky, V. M. J. *Phys. G* **1977**, *3*, 795.
(13) Ryzhikh, G. G.; Mitroy, J. *Phys. Rev. Lett.* **1997**, *79*, 4124.
(14) Hammond, B. L.; Lester, W. A., Jr.; Reynolds, P. J. *Monte Carlo methods in ab initio quantum chemistry*, 1st ed.; World Scientific: Singapore, 1994.
(15) Bressanini, D.; Mella, M.; Morosi, G. *J. Chem. Phys.* **1998**, *109*, 1716.
(16) Bubin, S.; Adamowicz, L. *J. Chem. Phys.* **2004**, *120*, 6051.
(17) Frolov, A. M.; Smith, V. H., Jr. *Phys. Rev. A* **1997**, *55*, 2662.
(18) Strasburger, K. *Chem. Phys. Lett.* **1996**, *253*, 49.
(19) Buenker, R. J. In *Proceedings of the Workshop on Quantum Chemistry and Molecular Physics*; Burton, P. G., Ed.; University of Wollongong Press: Wollongong/Australia, 1980; p 1.5.1. Buenker, R. J. In *Current Aspects of Quantum Chemistry*; Carbo, R., Ed.; Elsevier: Amsterdam, 1982; Vol. 21, p 81. Buenker, R. J.; Philips, R. A. *THEOCHEM* **1985**, *123*, 291 .
(20) Krebs, S.; Buenker, R. J. *J. Chem. Phys.* **1995**, *103*, 5613.
(21) Buenker, R. J.; Krebs, S. In *Recent Advances in Multireference Methods*; Hirao, K., Ed.; World Scientific Singapore, 1999; p 1.
(22) Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1974**, *35*, 33. Buenker, R. J.; Peyerimhoff, S. D. *Theor. Chim. Acta* **1975**, *39*, 217. Buenker, R. J.; Peyerimhoff, S. D.; Butscher, W. *Mol. Phys.* **1978**, *35*, 771.
(23) Tachikawa, M.; Buenker, R. J.; Kimura, M. *J. Chem. Phys.* **2003**, *119*, 5005.
(24) Tachikawa, M.; Buenker, R. J.; Kimura, M. *J. Chem. Phys.* **2004**, *121*, 9191.
(25) Strasburger, K. *Struct. Chem.* **2004**, *15*, 415.
(26) King, H. F.; Dupuis, M. *J. Comput. Phys.* **1976**, *21*, 144
(27) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69; **1960**, *32*, 179.
(28) Tinkham, M. *Group Theory and Quantum Mechanics*; McGraw-Hill: New York, 1964; p 162.
(29) Davidson, E. R. *J. Chem. Phys.* **1975**, *17*, 87. Davidson, E. R. *Int. J. Quantum Chem.* **1974**, *8*, 83.
(30) Mella, M.; Morosi, G.; Bressanini, D.; Elli, S. *J. Chem. Phys.* **2000**, *113*, 6154.
(31) Mella, M.; Chiesa, S.; Morosi, G. *J. Chem. Phys.* **2002**, *116*, 2852.
(32) Strasburger, K. *J. Chem. Phys.* **1999**, *111*, 10555.
(33) Strasburger, K. *J. Chem. Phys.* **2001**, *114*, 615.
(34) Davidson, E. R. In *The World of Quantum Chemistry*; Daudel, R., Pullman, B., Eds.; Reidel: Dordrecht, 1974; p 17.
(35) Hirsch, G.; Bruna, P. J.; Peyerimhoff, S. D.; Buenker, R. J. *Chem. Phys. Lett.* **1977**, *52*, 442.
(36) Knowles, D. B.; Alvarez-Collado, J. R.; Hirsch, G.; Buenker, R. J. *J. Chem. Phys.* **1990**, *92*, 585.
(37) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007.
(38) Tachikawa, M.; Shimamura, I.; Buenker, R. J.; Kimura, M. *New Directions in Antimatter Chemistry and Physics*; Surko, C. M., Gianturco, F. A., Eds.; Kluwer Academic: Dordrecht, 2001; Chapter 23, p 437.
(39) Cencek, W.; Rychlewski, J. *Chem. Phys. Lett.* **2000**, *320*, 549.
(40) Schafer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.
(41) Feller, D.; Glendening, E. D.; Woon, D. E.; Feyereisen, M. W. *J. Chem. Phys.* **1995**, *103*, 3526.
(42) Hurley, M. M.; Pacios, L. F.; Christiansen, P. A.; Ross, R. B.; Ermler, W. C. *J. Chem. Phys.* **1986**, *84*, 6840.
(43) Tachikawa, M., unpublished results.
(44) LaJohn, L. A.; Christiansen, P. A.; Ross, R. B.; Atashroo, T.; Ermler, W. C. *J. Chem. Phys.* **1987**, *87*, 2812.