

Positron and positronium chemistry by quantum Monte Carlo.

V. The ground state potential energy curve of e^+LiH

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The potential energy curve of e^+LiH has been computed by means of diffusion Monte Carlo using explicitly correlated trial wave functions. This curve allows us to compute the adiabatic total and binding energies and the vibrational spectrum of e^+LiH , and the adiabatic positron affinity of LiH . Using these results, we discuss the possibility to detect spectroscopically e^+LiH in the gas phase, in order to have the first direct observation of a positron-containing system. © 2000 American Institute of Physics. [S0021-9606(00)30739-5]

I. INTRODUCTION

During the last few years efforts have been directed to obtain accurate information on a positron or a positronium atom bound to small atomic and molecular systems.¹ Among the more extensively studied complexes are the atomlike systems PsH , e^+He^3S , e^+Li , and APs, where A is a first row atom or a one- or two-valence electron atom.²⁻⁷

To the best of our knowledge, much less effort has been devoted toward carrying out accurate calculations for small and medium molecular systems,⁸⁻¹³ lithium hydride being the only system for which analytical calculations by explicitly correlated Gaussians (ECG) have been carried out.^{8,10-12} We believe this fact is due primarily to the difficulty to compute the electron-positron correlation energy by means of standard *ab initio* methods, as shown by Strasburger.^{10,12}

From the theoretical point of view, LiH represents the ideal test case to study correlation effects in molecular systems due to the small number of electrons and its ability to bind either an electron or a positron. As far as the binding of a positron is concerned, the first sound numerical demonstration of the stability of e^+LiH was given by Kurtz and Jordan⁹ by means of SCF calculations. Moreover, they explored the bottom of the potential energy curve, finding that the LiH equilibrium distance $R_e = 3.015$ bohr increases to $R_e = 3.165$ bohr upon attachment of a positron. Using similar SCF calculations, they computed a larger equilibrium distance, $R_e = 3.265$ bohr, for LiH^- . They discussed these different behaviors as a consequence of the fact that the positron orbital is more diffuse than the one of the excess electron. This fact might reduce the interaction between the positron and the electrons, inducing smaller changes of the electron distribution, and so a smaller increase of the equi-

librium distance. As a further consequence, the importance of a correlated description of the positron-electron relative motions should be smaller.

These conclusions were refuted by Strasburger¹⁰ by means of a configuration interaction (CI) calculation including single and double excitations on e^+LiH at the LiH equilibrium distance. He found the CI positron affinity (PA) of LiH to be 0.0170 hartree, nearly three times the SCF one, 0.0059 hartree, showing therefore the importance of a correlated description and the inaccuracy of the SCF wave function in describing positron-containing systems. Unfortunately, even for systems smaller than e^+LiH the CI method performs poorly with respect to the convergence toward the exact values of both the positron-electron correlation energy and the annihilation rate, i.e., the probability for a positron to "collide" with an electron.

In our previous works^{8,11} we computed energies [$-8.1037(4)$ hartree and $-8.1023(1)$ hartree], PA, and other observables for the ground state of e^+LiH at $R = 3.015$ bohr by means of quantum Monte Carlo methods and explicitly correlated wave functions. Our diffusion Monte Carlo (DMC) result for the PA, 0.0333(4) hartree, showed that even the CISD result by Strasburger is off by a factor of 2. Moreover, we found the annihilation rate for this system, 1.21(4) ns⁻¹, to be much smaller than for the PsH system, 2.38(4) ns⁻¹.

Recently, Strasburger¹² obtained an accurate value of -8.10485 hartree for the mean energy of e^+LiH at $R = 3.015$ bohr by means of explicitly correlated Gaussians (ECG). This value is slightly lower than our former energies, but that can be easily explained by the fact that our calculations were carried out employing the fixed node approximation in the diffusion Monte Carlo (FN-DMC) simulation. This introduces a variational approximation to the nodal surface for the system,¹⁴ so that the energy is always an upper bound to the exact one. Strasburger¹² computed an annihila-

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tion rate for this system equal to 1.26 ns^{-1} . The DMC value $1.21(4) \text{ ns}^{-1}$, calculated from the data of Ref. 11, is in good agreement with the ECG one,¹² and this fact shows the ability of DMC to compute accurately this observable for small systems. More interestingly, Strasburger found the ECG positron density and contact density, i.e., the probability to find a positron and an electron at the same point in space, to be quite different from the SCF ones. These facts again reflect the extreme importance of the positron–electron correlation to describe the physics of the positron-containing systems. The contact density is strongly peaked on the hydrogen nucleus, showing the electronic density around this position to be responsible for the annihilation process.

Although these results give interesting information about various aspects of the interaction of a positron with a molecular system, several other questions have to be answered before a complete understanding can be gained. Among these, it is interesting to explore the effect of the binding of the positron on the geometry of e^+ LiH, the dependence of the PA on the Li–H distance, and the change of the vibrational spectrum with respect to LiH.

In this work we present a numerical study of the potential energy curve for the ground state of the e^+ LiH system by means of the FN-DMC method. The energy values obtained at various distances allow us to find the minimum of the potential well and to compute the vibrational levels of this strongly anharmonic system.

Although the value of the dipole moment of LiH could be large enough to allow the existence of bound excited states, we concentrated our effort only on the Σ ground state since DMC is not well suited to compute excited states. Nevertheless, an investigation of the stability of the lowest excited state of a different symmetry, for example the first Π or Δ states, could be easily performed including the symmetry constraint, and could be a subject of a future work.

II. HAMILTONIAN, TRIAL WAVE FUNCTION FORM, AND MONTE CARLO SIMULATION

In the following the Latin n subscript denotes a nucleus, a Greek subscript denotes an electron, while the Latin p subscript denotes the positron.

In atomic units, the Hamiltonian operator (in the Born–Oppenheimer approximation) for a molecular system containing a positron has the form

$$\mathcal{H} = -\frac{1}{2} \left(\sum_{\nu}^N \nabla_{\nu}^2 + \nabla_p^2 \right) + V(\mathbf{R}), \quad (1)$$

where $V(\mathbf{R})$ is the Coulomb interaction potential,

$$V(\mathbf{R}) = -\sum_{n=1}^{N_{\text{nuc}}} \sum_{\nu=1}^N \frac{Z_n}{r_{\nu n}} + \sum_{n=1}^{N_{\text{nuc}}} \frac{Z_n}{r_{pn}} + \sum_{\mu < \nu}^N \frac{1}{r_{\mu\nu}} - \sum_{\nu}^N \frac{1}{r_{p\nu}}, \quad (2)$$

between the charged particles (i.e., the N electrons, the positron, and the N_{nuc} fixed nuclei of charge Z_n), and $\mathbf{R} = (\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{r}_p)$ is a point in configuration space.

To approximate the wave functions at different Li–H distances, we use a trial wave function of a product form: a

function of the electronic coordinates times a function of the positron coordinates and of the positron–electron distances:

$$\Psi_T = \text{Det}[\phi_{\alpha}] \text{Det}[\phi_{\beta}] e^{U(r_{\mu\nu})} \Omega(\mathbf{r}_p, r_{p\nu}); \quad (3)$$

$\phi_{\alpha, \beta}$ are orbitals and $e^{U(r_{\mu\nu})}$ is the electronic correlation factor used by Schmidt and Moskowitz in their works on atoms and ions.^{15,16} In Eq. (3),

$$\Omega(\mathbf{r}_p, r_{p\nu}) = \sum_{i=1}^{N_{\text{terms}}} c_i \Phi_i(\mathbf{r}_p, r_{p\nu}), \quad (4)$$

where^{17–19}

$$\Phi_i(\mathbf{r}_p, r_{p\nu}) = f_i(\mathbf{r}_p) \exp \left\{ k_{i,1} \sum_{\nu=1}^N r_{p\nu} - \sum_{n=1}^{N_{\text{nuc}}} k_{i,1+n} r_{pn} \right\}. \quad (5)$$

In this equation, $f_i(\mathbf{r}_p)$ is a function that contains explicitly the dependence on the spatial coordinates of the positron, \mathbf{k}_i is a vector of parameters for the i th term of the linear expansion. The last N_{nuc} components of this vector were forced to have only positive values for all the terms of the linear combination. This ensures having the correct long range decay for the positron part of the trial wave function, in order to be square integrable.

This trial wave function, which has the correct spin and space symmetry, describes the electron–electron and electron–positron correlation by means of the exponential parts depending explicitly on the electron–electron and electron–positron distances. This analytical form allows an accurate description of the correct behavior of the exact wave function at the coalescence point for equal and opposite sign charges. Satisfying the cusp conditions usually accelerates the convergence of the wave function²⁰ to the exact one, and reduces its complexity for a chosen accuracy. This is useful to reduce the computational cost of the optimization of the parameters in the trial wave function, which is usually a quite demanding task.

Although more flexible trial wave functions have been used to obtain accurate approximations of the ground state of the e^+ LiH system,¹¹ they have a greater computational cost per Monte Carlo step, and appear to be too expensive to be used for the calculation of a complete potential energy curve. In this work we do not require that flexibility as we are not interested in obtaining the dependency of the annihilation rate on the internuclear distance, but only the total energy of the system. We believe that the wave function described in Eq. (3) should possess a sufficiently good nodal surface to allow us to obtain accurately the energy by DMC, so we decided to use it here to guide all our calculations.

Since Monte Carlo methods are well described in the literature,¹⁴ we only summarize the main points relevant to this work. DMC samples the distribution $f(\mathbf{R}) = \Psi_T(\mathbf{R})\Psi_0(\mathbf{R})$, simulating the time-dependent Schrödinger equation in imaginary time as a diffusion equation having source and sink terms. We use the fixed node approximation to sample an antisymmetrized wave function. So, $\Psi_0(\mathbf{R})$ is the ground state wave function of the system with the same nodal surface of the trial wave function. If the ground state

has no nodes, or $\Psi_T(\mathbf{R})$ has the correct nodal structure, this equation gives the exact ground state energy; otherwise one obtains an upper bound to it.

To optimize the nonlinear parameters in the trial wave function, we minimized the function

$$\mu^2(E_r) = \frac{1}{N_{\text{conf}}} \sum_{j=1}^{N_{\text{conf}}} [\mathcal{H}_{\text{loc}}(\mathbf{R}_j) - E_r]^2, \quad (6)$$

$\{\mathbf{R}_j, j=1, N_{\text{conf}}\}$ being a set of N_{conf} fixed configurations sampled from Ψ_T^2 , and E_r is an approximation to the true value of the energy for the system. This method, proposed by Frost²¹ and Conroy,²² was described in detail by Umrigar *et al.*²³ and by Mushinski and Nightingale²⁴ and has been proved to be much more stable than the optimization of the energy itself, at least if a fixed sample of configurations is used.

III. MONTE CARLO RESULTS AND DISCUSSION

The ground state energy of $e^+\text{LiH}$ was computed by means of DMC simulations²⁵ for various nuclear distances, in order to obtain the potential energy curve of this system.

For the electronic part of the wave function, we used the basis set optimized by Cade and Huo²⁶ for LiH to obtain the molecular orbitals for each nuclear distance, while the standard 17 term correlation factor was employed to introduce the correlation between electrons. The correlation factor was roughly optimized for every nuclear distance by means of the minimization of μ^2 for the neutral system. Similarly, the \mathbf{k}_i nonlinear parameters of the trial wave function in Eq. (5) were optimized at each nuclear distance by minimizing the quantity in Eq. (6). During the optimization process a set of 5000 configurations was used; at every three or four optimization steps this ensemble was updated by means of a variational Monte Carlo (VMC) run. As noted in our previous work,⁸ for this system the VMC values of the PA have a very low accuracy, comparable with the PA obtained by means of SCF calculations. To obtain accurate values for the PA one has to rely on the ability of the DMC simulations to recover the whole electron–positron correlation energy. Thus we show only the DMC results in Table I. These were computed using a target population of 5000 walkers and a time step of $0.003 \text{ hartree}^{-1}$; their accuracy was tested by running a few simulations using a time step of $0.001 \text{ hartree}^{-1}$ and comparing results. These were found to be in statistical agreement. Figure 1 plots our DMC results together with the potential energy curve for the LiH molecule computed by Partridge and Langhoff²⁷ by means of CI calculations. To compare the two systems in a meaningful way, we shifted the LiH curve by the difference between the exact and computed asymptotic values of the energy of Li and H, namely 0.00519 hartree .

Turning to the dissociation of $e^+\text{LiH}$, both DMC⁵ and ECG² calculations on the fragments Li^+ , LiPs , PsH , and Li predict $\text{PsH} + \text{Li}^+$ to be the lowest-energy channel, the ECG energy being -8.06909 hartree . Despite the fact that the analytical form of our trial wave function, i.e., a determinant times a correlation factor, was not chosen to correctly reproduce the dissociation behavior of $e^+\text{LiH}$, and hence the

TABLE I. $e^+\text{LiH}$ FN-DMC energies versus the internuclear distance R .

R (bohr)	E (hartree)
2.00	-8.0207(1)
2.15	-8.0479(1)
2.25	-8.0614(1)
2.35	-8.0717(1)
2.50	-8.0847(1)
2.75	-8.0973(1)
3.25	-8.1060(2)
3.50	-8.1071(1)
3.75	-8.1056(1)
4.00	-8.1032(2)
4.50	-8.0978(1)
5.00	-8.0920(2)
6.00	-8.0846(2)
7.00	-8.0782(1)
8.00	-8.0752(1)
9.00	-8.0730(2)
10.00	-8.0717(3)
12.00	-8.0700(2)

nodal surfaces, ongoing toward large nuclear distances, Table I shows that the DMC energy for nuclear distances larger than 8 bohr seems to converge correctly to the asymptotic value. A short calculation at $R=15 \text{ bohr}$ was found in statistical agreement with the correct asymptotic value. We fitted the bottom of the potential well by means of a fifth-order polynomial in order to compute the equilibrium distance and the harmonic frequency of the system, obtaining $E_e = -8.1072(2) \text{ hartree}$, $R_{\text{eq}} = 3.458 \text{ bohr}$, and $\omega_{\text{eq}} = 921.2 \text{ cm}^{-1}$. This equilibrium distance is intermediate between the LiH experimental value of 3.015 bohr and the estimated LiH^+ value of 4.141 bohr .²⁸ Apparently the attraction of the positron on the valence electrons weakens the bonding strength. It is interesting to note that our equilibrium distance for $e^+\text{LiH}$ is larger by 0.29 bohr than the one predicted by Kurtz and Jordan using a SCF approach.⁹ Our previous result⁸ contradicted their claim on the small contribution of the electron–positron correlation energy to the total correlation energy of $e^+\text{LiH}$, and the present result highlights the importance of a correlated description of the system, even for the bond length. Therefore, we must conclude that the SCF

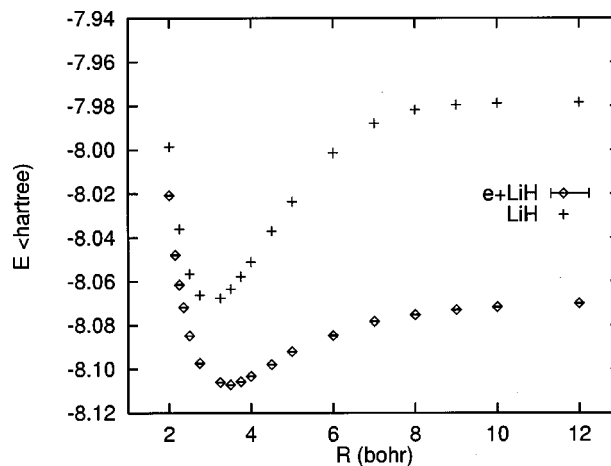


FIG. 1. The $e^+\text{LiH}$ and LiH potential energies.

method does not appear to be a useful tool to study and describe positron-containing systems, not even for qualitative information.

Our calculations of the dissociation energy of e^+LiH predict a value of 0.0381(1) hartree, i.e., more than two times smaller than the dissociation energy of LiH. This fact, together with the larger equilibrium distance we obtained, seems to suggest the presence of a fundamental difference between the electronic structures of LiH and e^+LiH , and between the mechanisms that are responsible for the binding in the two systems. Specifically, we believe e^+LiH to be bound by means of the charge-induced dipole interaction between Li^+ and PsH. Instead, in LiH the ionic Li^+H^- structure contributes to the binding near the equilibrium distance. This is supported by the DMC electron and positron densities we sampled during the simulations. For e^+LiH near equilibrium we found the positron density to be localized near the H nucleus and polarized outward in the bond region. Two electrons can be assigned to the Li atomic basin and two to the H one. This means that there is no charge transfer between the two asymptotic fragments Li^+ and PsH when they approach each other: they retain their identity although PsH is strongly polarized.

Let us consider the alternative channel for e^+LiH to dissociate into LiH and e^+ . The ground state energy for LiH is $-8.0704(1)$ hartree at the equilibrium distance 3.015 bohr, a result obtained by a DMC simulation.²⁹ This value is lower than the sum of the energy of PsH and Li^+ by 0.0013(1) hartree. However, adding the zero-point energy of this system, 0.0031 hartree, as computed using the potential energy curve of Partridge and Langhoff,²⁷ a nonadiabatic energy of $-8.0673(1)$ hartree is obtained for the neutral molecule, i.e., 0.0018(1) hartree above the PsH plus Li^+ dissociation threshold. This fact means that vibrational excitations of the molecule cannot transform e^+LiH into LiH by losing the positron, since these would lead the complex into the Li^+PsH dissociation channel. In order to free the positron from the complex, direct excitation of the electronic and positronic part of the molecule must be pursued. This result disagrees with the one in Ref. 9 that was obtained by means of standard SCF calculations.

Using the energy results shown in Table I, we interpolated the potential energy curve by means of cubic spline functions and solved the nuclear Schrödinger equation to compute the rovibrational levels of the e^+LiH system.³⁰ In Table II we show the results for the nuclear angular momentum $J=0$, together with the vibrational level spacings of LiH computed by Partridge and Langhoff.²⁷ From our results we obtain a zero-point energy of 0.0017(1) hartree, i.e., a nonadiabatic energy of $-8.1055(1)$ hartree for the positronic system. Using this result and the nonadiabatic energy of LiH, the nonadiabatic PA of the lithium hydride turns out to be 0.0382(2) hartree. This result can be compared with the nonadiabatic values computed by Mitroy and Ryzhikh³¹ by means of ECG functions, 0.0225 and 0.0320 hartree, obtained employing, respectively, the all-electron and the fixed-core version of the stochastic variational method (SVM). As Mitroy and Ryzhikh stated in their article,³¹ both their values seem not to be converged to the ground state

TABLE II. Energies and level spacings of the vibrational states of e^+LiH ($J=0$) and LiH.

ν	E^{e^+LiH} (hartree)	$E_{\nu+1}^{e^+LiH} - E_{\nu}^{e^+LiH}$ (cm^{-1})	$E_{\nu+1}^{LiH} - E_{\nu}^{LiH}$ (cm^{-1})
0	-8.105	879	1352
1	-8.101	830	1309
2	-8.097	773	1266
3	-8.093	705	1223
4	-8.090	625	1180
5	-8.087	556	1135
6	-8.085	513	1091
7	-8.082	485	1050
8	-8.080	446	1009
9	-8.078	392	969
10	-8.076	336	929
11	-8.075	277	888
12	-8.074	236	800
13	-8.073		751

solution due to the intrinsic difficulty in dealing with five- and seven-particle systems. This fact might explain the difference between our result and their nonadiabatic PA. Although this fact precludes us the possibility to test the accuracy of the Born–Oppenheimer approximation as a first-order approximation for dealing with molecules containing a positron, our calculations confirm their numerical results representing the first definitive demonstration that the e^+LiH system is stable. An insight about the accuracy of our PA can be obtained using the difference between the DMC and ECG¹² energy values computed at the nuclear distance of 3.015 bohr. This difference, namely 0.0011(4) hartree, is due to the fixed node approximation and can be assumed to be constant, at least in the range of nuclear distances around the potential minimum of the energy curve. This is equivalent to assuming that the nodal surfaces of the trial wave functions for small geometry changes have similar “accuracy” in describing the electronic part of the system. This assumption in our experience has been verified in many calculations on less exotic molecules. These ideas lead us to estimate the error in our PA to be of the order of 1 mhartree.

As far as the vibrational spectrum is concerned, our results (cf. Table II) show a large decrease of the level spacing for e^+LiH relative to LiH due to the shallower well of the positronic system. The fundamental transition is red-shifted by about 500 cm^{-1} . This fact should allow an easy detection of e^+LiH from experiments. The calculation of the vibrational spectrum gave two bound states beyond the ones reported in Table II. Since we believe their values were not fully converged, even with the largest basis set we could use, we decided to omit these from the reported list.

Interesting information can be extracted about the polarizability of PsH from the results in Table I. Asymptotically, i.e., for large nuclear distances, the analytical form of the e^+LiH potential energy curve should be

$$E(R) = -\frac{\alpha_{PsH}}{2R^4} + E_{PsH} + E_{Li^+}, \quad (7)$$

where α_{PsH} is the polarizability of the PsH system. We fitted this form to the energy values at $R=9, 10,$ and 12 bohr, obtaining $\alpha_{PsH}=49(2)$ hartree bohr⁴. This value is much

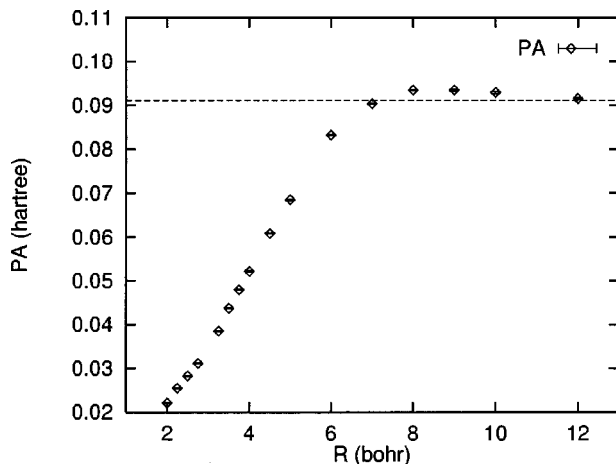


FIG. 2. LiH vertical positron affinity. The dashed line is the asymptotic value.

smaller than the one obtained by Le Sech and Silvi,³² namely 123 hartree bohr⁴, employing a variational procedure and explicitly correlated wave functions.

The difference between the two results appears to be too large to be explained by only invoking the different accuracies of the two methods. To solve this matter we are carrying out more accurate calculations on the polarizability of the PsH system using DMC in conjunction with finite-field techniques and perturbation theory.

In Fig. 2, we show the vertical PA computed for various distances of the Li and H nuclei. Asymptotically this quantity should converge to the value $PA(H^-) - IP(Li) + EA(H) = 0.0911$ hartree. Our results for R larger than 8 bohr seem to satisfy this requirement. It is interesting to notice that PA as a function of R does not appear to be monotonic. We believe this feature can be justified in terms of the different asymptotic laws of the potential energy curves of LiH and e^+LiH , i.e., the different exponents n in $1/R^n$ of the van der Waals expansion for large R . In fact, we were able to reproduce the nonmonotonicity fitting the PA values for $R = 7, 8, 9,$ and 10 by a simple three-term polynomial of the inverse distance with $n = 4, 6,$ and 8 . Ongoing toward smaller distances, since the PA represents the difference in leptonic energy between the two systems, this quantity should converge to the PA of Be. Unfortunately, it does not appear an easy task to extend our curve to smaller distances, primarily due to the worsening of the quality of the nodal surface of the SCF part of the trial wave function. It appears unable to reproduce the correct form for the Be atom. To explore this region one should use at least a multiconfigurational function to introduce the static correlation needed to correctly describe the Be atom.

IV. CONCLUSIONS

In this paper we computed the potential energy curve for the e^+LiH system in its ground state by means of the DMC method. Comparing our results with the energy value obtained by means of ECG¹² at the nuclear separation of $R = 3.015$ bohr, we estimate our curve to possess chemical accuracy, the difference between our value and the exact one

being of the order of 0.001 hartree. Vertical, adiabatic, and nonadiabatic PA should have the same accuracy. Using our energy results, we were able to predict the equilibrium geometry, the binding energy, and the vibrational spectrum of this system. The latter is especially important in the quest for an experimental signature of positron-containing systems different from the angular correlation annihilation radiation (ACAR) spectrum and the $\Gamma_{2\gamma}$ annihilation rate commonly accessed experimentally. The vibrational spectrum represents a possibility to directly detect the existence and properties of this system without relying on the indirect information that the ACAR spectrum and the $\Gamma_{2\gamma}$ give. Although this represents an attractive possibility, one should notice that the direct formation of e^+LiH by adding e^+ to the LiH molecule would cause the dissociation of the complex into Li^+ and PsH, since the PA is larger than the binding energy of the two fragments. This fact means that, to stabilize e^+LiH , a third body must be present to dissipate the excess energy, in order to provide the opportunity for the complex to remain bound. A possibility we feel worthy of investigation is to prepare the complex $LiH + Rg$ ($Rg = Ne, Ar, Kr$) so that the rare gas can leave the complex after the attachment of the positron with the excess of energy as kinetic energy. However, since infrared spectroscopy does not possess high sensitivity, it remains to solve the problem of obtaining a sufficient concentration of e^+LiH in the reaction chamber in order to be detected.

Although in this work we address most of the important features of the e^+LiH system, we believe there is still a question to be answered, namely the dependence of the annihilation rate $\Gamma_{2\gamma}$ on the nuclear separation. In our previous work on e^+LiH ¹¹ we made a first attempt to calculate this quantity. Comparing our result with the one obtained by Strasburger by means of ECG functions¹² it appears possible to compute accurate values of $\Gamma_{2\gamma}$ by DMC. Unfortunately that calculation, carried out employing explicitly correlated functions, was quite expensive. Any attempt to carry out an exploration for various internuclear distances is still out of the question. Nevertheless, both the results by Strasburger and ours show that the electron density of the Li^+ fragment does not play a crucial role in the annihilation since it overlaps only slightly with the positron density, at least for nuclear distances larger than 3.015 bohr. This fact allows one to avoid dealing explicitly with the core electrons by introducing a model potential or a frozen core approximation.³¹ These approximations reduce the computational cost of the optimization of the trial wave functions and of the simulations needed to compute the various observables. We are currently carrying out calculations employing this approach to explore the behavior of $\Gamma_{2\gamma}$ versus the internuclear distance.

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