PHYSICAL REVIEW A VOLUME 10, NUMBER 3 SEPTEMBER 1974

Binding of positrons to atoms

Sidney Golden and Irving R. Epstein*
Department of Chemistry, Brandeis University, Waltham, Massachusetts 02154

(Received 8 May 1974)

Necessary conditions for the existence of bound states for *positron-atom systems* are derived in terms of an adiabatic-type approximation by assuming that (i) their mutual potential energy has the form of a Morse potential and (ii) the first ionization energy of the atom exceeds the binding energy of an electron to a unit charge of infinite mass. Use is then made of the potential energies of the appropriate *proton-atom systems*, which have been determined by *ab initio* calculations or fitted to spectral or scattering data, to investigate the seven positron-atom systems to which the present theory is applicable. It is concluded that helium, nitrogen, and neon, in their ground states, should be incapable of binding positrons. Binding of positrons to hydrogen, oxygen, argon, and krypton, in their ground states, is not precluded by the theory, but the binding to krypton seems most likely.

I. INTRODUCTION

There has been much interest in recent years in the chemistry of so-called "new atoms"[1] in which protons or electrons are replaced by other fundamental particles of equal charge, such as positrons or mesons. The existence of some of these species as well as the analysis of many experiments which involve the interaction of positrons with matter[2,3] depends crucially upon whether or not there exist bound states of certain positron-atom systems.

A basic approach to determining the existence and nature of bound positron-atom states is to solve, in some suitable approximation scheme, the Schrödinger equation for the positron-atom system. A self-consistent-field theory of one-positron many-electron systems has been developed by Schrader,[4] although application of this method to large systems may well prove prohibitively expensive. Furthermore, in view of the notorious difficulty of the Hartree-Fock method in predicting the sign of the dissociation energy of many molecules,[5] predictions of the existence of bound positron-atom states which result from such a theory must be regarded with caution. The same caution applies to Hylleraas-type and other variational calculations.[6]

Another approach to the question of positron-atom binding is to seek upper or lower bounds to the number of bound states of the system. In this way, it may be possible to show that a system cannot have any bound states or that it must (or may) possess one or more bound states. Considerable progress has been made in obtaining upper bounds on the number of bound states (and hence, necessary conditions for the existence of any bound states) for a system consisting of a single particle subject to a spherically symmetric potential $V(r)$.[7,8] Gertler, Snodgrass, and Spruch[9] have derived, within an adiabaticlike approximation, necessary conditions for the existence of bound states of a variety of systems. Sufficient conditions for the existence of N bound states for a system may be derived from the Hylleraas-Undheim theorem.[10]

In spite of the array of theoretical methods noted above, little if anything is known about the existence or nonexistence of bound positron-atom species. In this paper we suggest how available *experimental* data on *proton-atom* interactions may be utilized to predict the nonexistence of positron-atom bound states. Subject to certain assumptions about the form of the proton-atom and positron-atom potentials, our approach makes use of an adiabatic-type approximation to yield necessary conditions for the existence of bound states. The use of experimentally determined potentials enables us to study more complex systems as easily as H-e^+ and He-e^+, which have been the major subjects of previous theoretical investigations.

In Sec. II we outline our approach and show how it is related to previous work.[7-9] The technique is then applied to a number of atoms and it is shown that certain of these should be incapable of supporting a positron-atom bound state. Finally, we discuss the sensitivity of our results to the choice of potentials and parameters and we suggest some limitations and possible extensions.

II. A NECESSARY CONDITION FOR POSITRON BINDING TO ATOMS

For generality, we will consider a singly charged positive particle and an N-electron neutral atom whose nucleus is fixed in space.[11] Then, expressed in atomic units, the Hamiltonian of the system can be taken as

$$H = H_{\text{atom}} + \frac{\vec{p}^2}{2m} - \sum_{k=1}^{N} \frac{1}{|\vec{r}_k - \vec{r}|} + \frac{N}{|\vec{r}|} , \qquad (1)$$

where $\vec{r}$, $\vec{p}$, and m refer to the position, momentum, and mass of the positive particle; all distances are measured from the nucleus of the atom. We presume that the system has a ground-state energy eigenvalue E_0 that is determined by

$$H|\psi_0\rangle = E_0 |\psi_0\rangle . \qquad (2)$$

In the extended Born-Oppenheimer (BO) approximation[12,13] there is a corresponding smallest energy eigenvalue, $E_0(\text{BO})$, that is determined by the pair of equations

$$\left(H_{\text{atom}} - \sum_{k=1}^{N} \frac{1}{|\vec{r}_k - \vec{r}|} + \frac{N}{|\vec{r}|}\right) |\psi_0(\vec{r}_k ; \vec{r})\rangle = V_{\text{BO}}(r) |\psi_0(\vec{r}_k ; \vec{r})\rangle \qquad (3)$$

and

$$[\vec{p}^2/2m + V_{\text{BO}}(r)] \, |\varphi_0(\vec{r})\rangle = E_0\,(\text{BO}) \, |\varphi_0(\vec{r})\rangle . \qquad (4)$$

The basic relation we use here is the Brattsev-Epstein[14,15] result that

$$E_0 \geq E_0\,(\text{BO}) . \qquad (5)$$

To do so, we let $E_{0,d}$ be the energy eigenvalue that corresponds to the threshold of dissociation of the positive particle and $E_{0,d}$ (BO) the analogous quantity determined by the extended Born-Oppenheimer approximation. Then Eq. (5) yields

$$\begin{aligned} E_{0,d} - E_0 &\leq E_{0,d} - E_0\,(\text{BO}) \\ &= [E_{0,d}\,(\text{BO}) - E_0\,(\text{BO})] \\ &\quad + [E_{0,d} - E_{0,d}\,(\text{BO})] . \end{aligned} \qquad (6)$$

When the first ionization energy of the atom exceeds that of a hydrogen atom of infinite mass, both $E_{0,d}$ and $E_{0,d}$ (BO) are the same and refer to a stationary, bare singly charged positive particle that is dissociated from the atom. For such atoms—which we henceforth assume—we must have

$$E_{0,d} - E_0 \leq E_{0,d}\,(\text{BO}) - E_0\,(\text{BO}) , \qquad (7)$$

so that the extended Born-Oppenheimer approximation provides an upper bound to the actual binding energy of the particle: the particle will be bound to the atom only if it is likewise "Born-Oppenheimer-bound." This forms a basis for determining when *an absence of binding* is to be expected between positrons and various atoms.[9]

Since $V_{\text{BO}}(r)$ is evidently independent of the mass of the positive particle, it may be estimated from appropriate spectroscopic and scattering properties of proton-atom systems—to the extent that they are adequately describable in terms of the extended Born-Oppenheimer approximation. In order to exploit Eq. (7) it is then necessary to solve Eqs. (3) and (4), a nontrivial matter. However, we can adapt the inequality to obtain another one which has the main feature of being easy to apply. We assume that it is possible to find a function $V_M(r)$ such that

$$V_M(r) \leq V_{\text{BO}}(r), \quad V_M(\infty) = V_{\text{BO}}(\infty) . \qquad (8)$$

Then Eq. (4) can be seen to yield

$$\begin{aligned} E_0\,(\text{BO}) &= \langle \varphi_0 | \frac{\vec{p}^{\,2}}{2m} + V_M(r) | \varphi_0 \rangle \\ &\quad + \langle \varphi_0 | V_{\text{BO}}(r) - V_M(r) | \varphi_0 \rangle \\ &\geq \langle \varphi_0 | \frac{\vec{p}^2}{2m} + V_M(r) | \varphi_0 \rangle \\ &\geq E_0(M) , \end{aligned} \qquad (9)$$

where $E_0(M)$ is the lowest energy eigenvalue of the modified Hamiltonian in which $V_M(r)$ replaces $V_{\text{BO}}(r)$. In view of the asymptotic behavior assumed for $V_M(r)$, we can safely conclude that the modified Hamiltonian has a threshold of dissociation of the positive particle $E_{0,d}(M)$ which is the same as $E_{0,d}$ (BO) and $E_{0,d}$. As a result, Eq. (7) yields

$$\begin{aligned} E_{0,d} - E_0 &\leq E_{0,d}\,(\text{BO}) - E_0\,(\text{BO}) \\ &\leq E_{0,d}\,(M) - E_0(M) . \end{aligned} \qquad (10)$$

Provided that a $V_M(r)$ can be found that satisfies Eq. (8), the particle will be bound to the atom only if it is likewise bound in the modified potential.

For reasons of analytic simplicity, we next represent $V_M(r)$ by a Morse potential[16] in which the asymptotic condition of Eq. (8) is satisfied. It is

$$V_M(r) = D(e^{-2a(r - r_0)} - 2e^{-a(r - r_0)}) + E_{0,d}(M) , \qquad (11)$$

where D is the minimum value of the potential and r_0 and a are parameters determined by the location of the minimum and the curvature there. Although it is likely that Eq. (11) will not precisely satisfy Eq. (8) everywhere, it will certainly do so for sufficiently small values of r; for values of r exceeding r_0, deviations from Eq. (8) can be expected to be small.[17] As is well known, many diatomic molecules are reasonably well described by such potentials, which have been fitted to appropriate experimental data. For further simplification, we suppose that the radial part of the Schrödinger's equation involving $V_M(r)$ can be extended to $(-\infty)$, as is usually done; this enables the energy eigenvalues arising from Eq. (11), for states of zero angular momentum, to be given in closed form.[17] The lowest such eigenvalue is demonstrably not greater than $E_0(M)$, so that Eq. (10) leads to the inequality (all quantities being expressed in atomic units)

$$E_{0,a} - E_0 \leq D[1-(a^2/8mD)^{1/2}]^2 , \tag{12}$$

provided that

$$8mD/a^2 \geq 1 . \tag{13}$$

This condition is necessary for the Morse potential to be capable of supporting at least one bound state. To the extent that the Morse potential adequately satisfies Eq. (8), the same condition is necessary for actual binding of the positive particle to the atom under consideration.

Because the problem of determining necessary conditions for the existence of a bound state has received attention in both general terms[7,8,10] and in connection with positron-binding,[9] it will be useful to compare the condition expressed by Eq. (13) with the necessary condition of binding given by Schwinger.[8] For a particle of mass m to be bound in a spherical potential $V(r)$, in a state of zero angular momentum, it is necessary that

$$2m \int_0^\infty dr\, r\, V_{(-)}(r) \geq 1 , \tag{14}$$

where

$$\begin{aligned} V_{(-)}(r) &\equiv |V(r)| , & V(r) &< 0 \\ &= 0, & V(r) &\geq 0 . \end{aligned} \tag{15}$$

If $V(r)$ is identified with the radially dependent part of $V_M(r)$ of Eq. (11), the necessary condition expressed by Eq. (14) becomes

$$(8mD/a^2)(\tfrac{3}{4} - \tfrac{1}{2}\ln 2 + \tfrac{1}{2}ar_0) \geq 1$$

or

$$\frac{8mD}{a^2} \geq \frac{1}{0.403 + 0.5\,ar_0} , \tag{16}$$

similar in form to Eq. (13). Since the values of ar_0 for the diatomic hydride ions to be considered here appear to appreciably exceed unity, the two criteria are not identical. In such cases, Eq. (13) expresses a stronger necessary condition for the existence of a bound state for the prescribed potential than does Eq. (16).[18]

By setting m equal to unity, the previous expressions are immediately pertinent to the question of interest here—the binding of positrons to atoms. To the extent that the restrictions of Eq. (8) may sometimes not be satisfied by a Morse potential, the necessary conditions which have been obtained lack the absolute rigor which we should like them to have. This limitation is compensated for by their easy application.

III. APPLICATION TO POSITRON-ATOM SYSTEMS

The criterion of Eq. (13) is, as noted previously, applicable only to atoms whose first ionization energy equals or exceeds that of a hydrogen atom of infinite mass. There are only seven elements which satisfy this requirement: hydrogen, nitrogen, oxygen, helium, neon, argon, and krypton.

Estimates of the parameters a, D, and r_0 in the Morse potentials [Eq. (11)] for these atoms may be obtained from three sources. These are (i) spectroscopic experiments, in which measurements are made of the electronic and vibrational energy levels of the ion AH^+; (ii) scattering experiments, in which data on the elastic scattering of protons by A atoms are inverted to yield information about the AH^+ potential; and (iii) *ab initio* calculations of the Born-Oppenheimer energies of AH^+ at a number of internuclear distances.

A. Hydrogen

Data relevant to the H_2^+ potential are available from both spectroscopic measurements and theoretical calculations, with the latter expected to be somewhat more reliable for this one-electron system. Herzberg[19] gives values for the *dissociation energy* D_0, the *vibrational constant* ω_e, and the internuclear distance at the potential minimum r_0, obtained from the experimental results of Richardson.[20] These values permit a determination to be made of the Morse-potential parameters.[21]

Application of Eqs. (13) and (16) to Herzberg's values for H_2^+ yields the results shown in the first row of Table I. We see that both criteria allow the species H-e^+ to be bound, and that the present criterion [Eq. (13)] imposes more stringent requirements for binding than does the Schwinger criterion [Eq. (16)].

Particularly in the case of H_2^+, where only a very limited amount of spectroscopic data is available, the parameters a, D, and r_0 may be expected to be known rather imprecisely. The second row of Table I contains values for these quantities calculated by Hellmann[22] from the spectroscopic tables of Sponer.[23] Comparison of the two sets of spectroscopic data affords both an estimate of the reliability of the parameters and some assurance that typical variations in the data or in their analysis do not change the qualitative conclusions drawn from the criteria for binding.

The potential curve for H_2^+ may be calculated

TABLE I. Data relating to the binding of positrons to some atoms A.

A	Source of data	D (a.u.) (AH^+)	a (a.u.$^{-1}$) (AH^+)	r_0 (a.u.) (AH^+)	$\frac{8mD}{a^2}$ [a]	$\frac{1}{0.403+0.5\,ar_0}$
H	Spectroscopic [b]	0.103	0.699	2.00	1.69	0.907
H	Spectroscopic [c]	0.102	0.683	2.02	1.75	0.915
H	Calculated [d]	0.103	0.720	2.04	1.59	0.879
H	Calculated [e]	0.103	0.762	2.04	1.42	0.847
H	Calculated [f]	0.103	0.683	2.04	1.77	0.909
N	Spectroscopic [g]	0.136	1.06	2.04	0.968	0.673
N	Calculated [h]	0.125	1.19	1.98	0.706	0.632
O	Spectroscopic [i]	0.168	0.964	1.95	1.39	0.744

[a] Reference 18.
[b] References 19 and 20.
[c] References 22 and 23.
[d] Least-squares fit of 74 points (Ref. 25) ($1.15 \le r \le 20$); three parameters.
[e] Least-squares fit of 18 points (Ref. 25) ($1.15 \le r \le r_0$); one parameter.
[f] Least-squares fit of 57 points (Ref. 25) ($r_0 \le r \le 20$); one parameter.
[g] Reference 30.
[h] Reference 29.
[i] References 31 and 32.

to a high degree of accuracy within the Born-Oppenheimer approximation, since the Schrödinger equation for this system is separable in confocal elliptical coordinates.[24] We have employed a nonlinear least-squares fitting procedure to approximate the accurate numerical results thus obtained by Wind[25] by Morse curves of the form of Eq. (11). In order to obtain reasonable fits to the data, it was necessary to discard the region of very small internuclear distances, since the Morse potential cannot be expected to describe accurately configurations in which the nuclear repulsion is the dominant energy term.

Table I gives the parameters obtained by a least-squares fit of Wind's data for the region in which $V_M(r)$ in Eq. (11) is less than the dissociation energy $E_{0,d}(M)$. Again we see that binding of a positron to a hydrogen atom is not ruled out by either criterion.

While D and r_0 appear relatively insensitive to the details of the fitting procedure, the parameter a does depend significantly upon the relative weight given to various parts of the curve. In order to obtain an estimate of the error inherent in the fitting procedure, we carried out two other calculations in which D and r_0 were fixed and only a was allowed to vary. Adopting a procedure suggested by the modified Morse curves used by Henglein *et al.*[26] in analyzing scattering data, we obtained the best value of a for describing the potential in the small-r region ($1.15 \le r \le r_0$), and an analogous value for the large-r region ($r_0 \le r \le 20$). These procedures produced changes in a of 5 to 6% in opposite directions, but again, as shown in the Table, our conclusions about binding remain unchanged.

These conclusions are completely in accord with those of Gertler, Snodgrass, and Spruch,[9] who have made direct use of a Born-Oppenheimer potential determined for H_2^+ to estimate E_0 (BO) of Eq. (4) and to evaluate the integral of Eq. (14). As a result of the small binding energy they obtained for H-e^+, they suggested that it is almost certainly unbound even though they were unable to prove that contention (as are we). However, in a later paper Aronson, Kleinman, and Spruch[27] have employed a potential that is adiabatic only with respect to the *proton-positron distance*[28] and thereupon find that positron binding to a hydrogen atom is not possible.

B. Nitrogen

Data on NH^+, either experimental or theoretical are rather limited. Liu and Verhaegen[29] have carried out *ab initio* calculations on the ground ($X^2\pi$) state of this ion at a number of internuclear distances. Their results and the corresponding experimental parameters[30] are given in Table I.

In spite of the rather large differences between the theoretical and experimental values, the qualitative conclusions are identical: *the criterion of Eq. (13) predicts the species* N-e^+ *to be unbound, while the Schwinger criterion [Eq. (16)] makes no such prediction.* In this case, only the more stringent criterion allows us to rule out binding.

C. Oxygen

In Table I are presented the parameters obtained by Herzberg[31] from an analysis of spectroscopic data[32] on the band structure of OH^+. The species O-e^+ is allowed by both criteria, but the uncertainties in the data suggest a need for further experiments and/or a calculation of the OH^+ potential curve.

D. Helium

While no spectroscopic data appear to be available for hydride ions of the noble gases, scattering measurements have been performed on these species.[33] In particular, Henglein and co-workers[26] have investigated the scattering of protons by helium, neon, argon and krypton atoms. They have used a modification of Eq. (11) in an attempt to solve the difficult problem of inverting the scattering data to yield the internuclear potential function. Two Morse potentials are employed with different values of a, depending upon whether r is greater than or less than r_0. In most cases, the curvature parameter a for the large-r region is about 0.8 to 0.9 times that for the small-r region. This result is in good agreement with our own fits of the H_2^+ data (Table I).

If one uses the lower a value (i.e., for the large-r region) in constructing the V_M of Eq. (8), then the inequality expressed in that equation may be expected to hold. In Table II, we give the parameters obtained by Henglein *et al.*[34] for He-H^+ scattering. The values of D and r_0 obtained by Rich *et al.*[35] from scattering data are also included for comparison.

Like H_2^+, HeH^+ has been of considerable interest to theorists, principally because of its relatively small size. Many calculations have been performed, including several[36-42] that give Born-Oppenheimer potential curves. Results from some of these calculations are presented in Table II together with the extremely accurate D and r_0 values of Wolniewicz.[43] In spite of significant differences among the varous calculations and between the theoretical and experimental parameters, the conclusion is unambiguous. Helium atoms should be incapable of binding positrons.

Here also our conclusions are in accord with those of Gertler, Snodgrass, and Spruch.[9] However, Khare, Wallace, Bach, and Chodos[44] have carried out a variational calculation on He-e^+, with an opposite conclusion. This latter result which is in direct contradiction to our conclusion and that of others,[9,45] has been questioned by Lebeda and Schrader[46] on the grounds that (i) the variational functions used to describe the bound and unbound systems are not of comparable flexibility and (ii) the difference between two bounds is not itself a bound.

E. Neon

The scattering data for NeH^+ are summarized in Table II. Also given are two sets of parameters obtained from the *ab initio* calculation of Peyerimhoff,[39] the first by the Henglein *et al.*[34] modified-Morse-potential analysis, the second by our analysis of the spectroscopic quantities calculated by Peyerimhoff.[39] Again, in spite of sizeable variations among the various parameter sets, the conclusion that binding cannot occur remains unchanged.

F. Argon

The scattering experiments of Henglein *et al.*[26] afford the only complete set of data on the ArH^+ system (Table II). However, the good agreement of their values for D and r_0 with those obtained by both experimental[35] and theoretical[47] methods, together with the large value of $8mD/a^2$, suggest that further data are unlikely to yield a prediction of nonbinding of positrons to argon atoms with the present criterion.

G. Krypton

Only scattering data are available for Kr-H^+. The relatively deep, broad well implied by the large D and small a values suggests that of the atoms considered here, krypton should provide the most favorable environment for binding a positron. However, our criterion provides only necessary conditions for binding, and it may be dangerous to attach further quantitative significance to the values of $8mD/a^2$.

IV. DISCUSSION

It is encouraging to note that in every case presented here, regardless of variations in the experimental and theoretical parameters used, the conclusion reached as to the possibility or impossibility of binding remains unaffected. This suggests that our criterion is sufficiently insensitive to small variations in the data and in the method of their analysis that it may safely be applied even to relatively crude measurements. Certainly, errors in the determination of the dissociation energy D are unlikely to be large enough to affect any of our conclusions. The relatively greater sensitivity of the parameter a and the greater difficulty of measuring this quantity accurately are somewhat disturbing. Nevertheless, only in the case of the NH^+ spectroscopic data would a change of 15% in the value of a reverse our conclusions.

TABLE II. Data relating to the binding of positrons to noble-gas atoms *A*.

A	Source of data	D(a.u.) (AH^+)	a(a.u.$^{-1}$) (AH^+)	r_0(a.u.) (AH^+)	$\frac{8\vec{m}D}{a^2}$[a]	$\frac{1}{0.403+0.5\,ar_0}$
He	Scattering[b]	0.074 ± 0.004	1.28[c]	1.46 ± 0.04	0.361	0.748
He	Scattering[d]	0.080	···	1.41	···	···
He	Calculated[e]	0.059	1.56	1.480	0.194	0.642
He	Calculated[f]	0.070	1.68	1.432	0.198	0.623
He	Calculated[g]	0.071	1.56	1.446	0.234	0.653
He	Calculated[h]	0.071	1.49	1.455	0.256	0.673
He	Calculated[i]	0.067	1.60	1.444	0.209	0.642
He	Calculated[j]	0.066	1.52	1.464	0.229	0.660
He	Calculated[k]	0.078	1.50	1.446	0.277	0.672
He	Calculated[l]	0.074 94	···	1.463 24	···	···
Ne	Scattering[b]	0.084 ± 0.004	1.22[c]	1.87 ± 0.06	0.451	0.649
Ne	Scattering[d]	0.083	···	1.90	···	···
Ne	Calculated[h]	0.081	1.25[c] (1.52)[m]	1.83	0.415 (0.280)[m]	0.647 (0.557)[m]
Ar	Scattering[n]	0.148 ± 0.004	0.87[c]	2.48 ± 0.13	1.56	0.408
Ar	Scattering[d]	0.155	···	2.35	···	···
Ar	Calculated[o]	0.151	···	2.61	···	···
Kr	Scattering[b]	0.164 ± 0.004	0.72[c]	2.78 ± 0.11	2.53	0.713
Kr	Scattering[d]	0.17	···	2.9	···	···

[a] Reference 18.

[b] Reference 34.

[c] Modified morse potential (Ref. 26) value given for *a* is for the outer part of the curve ($r \geq r_0$) where the curvature is smaller.

[d] Reference 35.

[e] Reference 36.

[f] Reference 37.

[g] Reference 38.

[h] Reference 39.

[i] Reference 40.

[j] Reference 41.

[k] Reference 42.

[l] Reference 43.

[m] Values in parenthesis calculated from *a* value obtained from Peyerimhoff's spectral parameters.

[n] Reference 26.

[o] Reference 47.

While the limitation of the present method to only seven elements of the periodic table is rather severe, the possibility of treating krypton and xenon as easily as hydrogen and helium offers at least some compensation. In addition it may be possible to extend our approach to utilize proton-molecule scattering data[48] for obtaining bounds on the binding energies of positrons to relatively spherical molecules with sufficiently high first ionization energies.

Although we have been able to compare theoretical with spectroscopic and theoretical with scattering data, no system has come to our attention for which both sufficient spectroscopic and scattering data are available for parallel determinations of the Morse-potential parameters. Such a point of overlap might provide a useful check of both the present approach and of the inversion techniques which have been applied to the scattering data. It would seem that the ArH^+ and KrH^+ systems, which appear from the scattering experiments to be quite strongly bound, might provide interesting subjects for spectroscopic investigation.

As for experimental verification of the existence of bound positron-atom systems, our calculations clearly point to krypton as the most likely atom to bind a positron. The large value of $8mD/a^2$ and the fact that the upper bound[49] on the binding energy is twice as great (0.061 a.u. or 1.6 eV) for krypton as for any other atom, are certainly suggestive, if not conclusive. The next most likely candidate from a practical point of view appears to be argon.

The results we have obtained have explicitly dealt with the possibility of positrons being bound to atoms only when the latter are in their ground states. In the course of experiments designed to ascertain the existence of bound positron-atom states, it is conceivable that the atoms may be excited to states that differ appropriately from the ground state, e.g., have a different electronic spin. In such cases, the method which has been described could be used if the relevant data for the corresponding proton-atom system were available. Lacking such information, we are unable to preclude the possibility of positron binding in such cases. In fact, despite the negative results that we have obtained for helium, nitrogen, and neon, the possibility that excited states of these atoms may give rise to bound positron-atom states must not be lost sight of.

ACKNOWLEDGMENT

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. Partial support from the National Science Foundation (NSF-D Grant No. GU-3852) is also acknowledged.

---

*Camille and Henry Dreyfus Foundation Teacher-Scholar Grant Recipient, 1973–78.

[1] For a comprehensive review, see V. I. Gol'danskii and V. G. Firsov, Ann. Rev. Phys. Chem. 22, 209 (1971).

[2] S. J. Tao and J. H. Green, J. Chem. Soc. A 1968, 408 (1968).

[3] V. I. Gol'danskii, At. Energy Rev. 6, 3 (1968).

[4] D. M. Schrader, Phys. Rev. A 1, 1070 (1970).

[5] J. L. Whitten, Acc. Chem. Res. 6, 238 (1973).

[6] S. K. Houston and R. J. Drachman, Phys. Rev. A 7, 819 (1973).

[7] V. Bargmann, Proc. Natl. Acad. Sci. USA 38, 961 (1952).

[8] J. Schwinger, Proc. Natl. Acad. Sci. USA 47, 122 (1961).

[9] F. H. Gertler, H. B. Snodgrass, and L. Spruch, Phys. Rev. 172, 110 (1968).

[10] E. A. Hylleraas and B. Undheim, Z. Phys. 65, 759 (1930).

[11] The restriction to a nucleus fixed in space is mainly done for convenience, and may be relaxed by working in a center-of-mass representation for the system. The latter will give a slightly stronger necessary condition for positron binding than we later obtain.

[12] M. Born and R. Oppenheimer, Ann. Phys. (Leipz.) 84, 457 (1927).

[13] M. Born, Nachr. Akad. Wiss. Goett. Math.-Phys. 2, No. 6 (1951).

[14] V. F. Brattsev, Dokl. Akad. Nauk. SSSR 160, 570 (1965) [Sov. Phys.—Doklady 10, 44 (1965)].

[15] S. T. Epstein, J. Chem. Phys. 44, 836 (1966); 44, 4062 (1966).

[16] P. M. Morse, Phys. Rev. 34, 57 (1929). The modification in Eq. (11) merely reflects a choice of an energy origin that is appropriate to the present problem.

[17] See, in this connection, G. Herzberg, *Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules* (van Nostrand, Princeton, 1950), p. 99. For the systems of interest here, we are disregarding the long-range charge-induced dipole interaction.

[18] Note that Eq. (13) immediately yields the largest mass for which binding cannot occur, namely, $a^2/8D$. This is invariant to the location of the minimum of the Morse potential while, by contrast, increasing r_0 indefinitely means that Eq. (16) can then be satisfied for any m.

[19] G. Herzberg, *op. cit.*, p. 534.

[20] O. W. Richardson, Proc. R. Soc. Lond. 152, 503 (1935); Nuovo Cimento 15, 232 (1938).

[21] G. Herzberg, *op. cit.*, p. 101.

[22] H. Hellmann, *Einführung in die Quantenchemie* (Deuticke, Leipzig, 1937), p. 297.

[23] H. Sponer, *Molekülspektren und ihre Anwendung auf Chemische Probleme* (Springer, Berlin, 1935).

[24] O. Burrau, K. Dan. Vidensk. Selsk. Mat.-Fys. Medd 7, 1 (1927).

[25] H. Wind, J. Chem. Phys. 42, 2371 (1965).

[26] H.-U. Mittmann, H.-P. Weise, A. Ding and A. Henglein, Z. Naturforsch. A 26, 1112 (1971).

[27] I. Aronson, C. J. Kleinman, and L. Spruch, Phys. Rev. A 4, 841 (1971).

[28] See, in this connection, S. Golden, Phys. Rev. A 9, 530 (1974).

[29] H. P. D. Liu and G. Verhaegen, J. Chem. Phys. 53, 735 (1970).

[30] R. Colin and A. E. Douglas, Can. J. Phys. 46, 61 (1968).

[31] G. Herzberg, *op. cit.*, p. 561.

[32] F. W. Loomis and W. M. Brandt, Phys. Rev. 49, 55 (1936); L. N. Challacombe and G. M. Almy, Phys. Rev. 51, 63, 930 (1937).

[33] For a review and useful general discussion of these and related experiments, see H.-P. Weise, Ber. Bunsenges. Phys. Chem. 77, 578 (1973).

[34] H.-P. Weise, H.-U. Mittmann, A. Ding and A. Henglein, Z. Naturforsch. A 26, 1122 (1971).

[35] W. G. Rich, S. M. Babbio, R. L. Champion, and L. D. Doverspike, Phys. Rev. A 4, 2253 (1971).

[36] J. A. Keefer, J. K. SuFu, and R. L. Belford, J. Chem. Phys. 50, 1087 (1969).

[37] A. A. Evett, J. Chem. Phys. 24, 150 (1956).

[38] B. G. Anex, J. Chem. Phys. 38, 1651 (1963).

[39] S. Peyerimhoff, J. Chem. Phys. 43, 998 (1965).

[40] H. M. Michels and F. E. Harris, J. Chem. Phys. 39, 1464 (1963).

[41] J. D. Stuart and F. A. Matsen, J. Chem. Phys. 41, 1646 (1964).

[42] C. A. Coulson and W. E. Duncanson, Proc. R. Soc. Lond. A 165, 90 (1938).

[43] L. Wolniewicz, J. Chem. Phys. 43, 1087 (1965).

[44] H. C. Khare, P. R. Wallace, G. G. Bach, and A. Chodos, Can. J. Phys. 42, 1522 (1964).

[45] G. Oczkowski, thesis (University of Manitoba, 1961) (unpublished).

[46] C. F. Lebeda and D. M. Schrader, Phys. Rev. 178, 24 (1969).

[47] A. C. Roach and P. J. Kuntz, Chem. Commun. 1970, 1336.

[48] H.-U. Mittman, H.-P. Weise, A. Ding, and A. Henglein, Z. Naturforsch. A 26, 1282 (1971).

[49] May be obtained from Eq. (12).