Calculation of potential energy curves for the process
$C^{3+}(2l)+H(1s)\rightarrow C^{2+}(nln'l';{}^1L)+H^+$ using spin-coupled valence-bond theory

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Potential energy curves of ${}^1\Sigma^+$ symmetry have been calculated for the process $C^{3+}(2l)+H(1s)\rightarrow C^{2+}(nln'l';{}^1L)+H^+$ by means of the spin-coupled valence-bond theory. Very large basis sets of Slater functions have been used in order to describe reasonably well a large number of states. A total of eleven states has been examined, the asymptotic energies of which match the experimental values closely: errors are 0.02–0.9 eV over a range of 45 eV. The only exception is the $C^{2+}(2s\,3d;{}^1D)+H^+$ state where there is a discrepancy of 2 eV which we attribute to remaining deficiencies in the $3d$ basis set. The charge-transfer states $C^{3+}(2s;{}^2S)+H(1s)$ (state 7) and $C^{3+}(2p;{}^2P)+H(1s)$ (state 11) show very strongly avoided intersections with at least four other states. We conclude that charge-transfer studies of this system must take into account a minimum of five strongly coupled states. Later studies will concentrate on the ${}^3\Sigma^+$ states and on the radial couplings.

I. INTRODUCTION

Multicharged ions coexist with neutral species in plasmas produced by high-frequency photons or when a current of neutrals is injected into a magnetically confined plasma. The degree of penetration of a neutral hydrogen beam is very dependent on charge-transfer processes of the type

$$X^{(n+1)+}+H\rightarrow X^{n+}+H^+ .$$
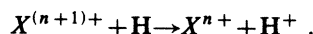
The X^{n+} ions are frequently produced in excited states and the resulting photon emissions

$$(X^{n+})^*\rightarrow X^{n+}+h\nu$$
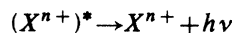
are potentially useful as a diagnostic probe. On the other hand, these radiation losses cool the plasma. The above processes may continue until X becomes electrically neutral or until it again becomes fully ionized; impurity ions may thus be very efficient cooling agents. Depending on the nature of the experiment, a variety of elements may be present—such as carbon from residual CO_2 or from steels containing the element. Charge transfer in collisions of multicharged ions with H or He also plays a major role in the determination of the thermal and ionization structure of a wide variety of astrophysical plasmas. Elements especially important in this respect, because of their relative abundance, include carbon, nitrogen, and oxygen.

A variety of measurements have been performed for the charge-transfer process $C^{3+}+H\rightarrow C^{2+}+H^+$. Total cross sections at low energies[1] decrease to a value of 6×10^{-16} cm^2 at 250 eV/amu. High-energy results[2] indicate total cross sections of about 1.6×10^{-15} cm^2. These two sets of results were brought into apparent harmony by *ab initio* quantal calculations,[3] but recent measurements have cast doubt upon this. In particular, observation of photon emission from newly formed C^{2+} ions has led to the measurement of individual state-selected charge-transfer cross sections in the C^{3+}-H(1s) system.[4] These new measurements are in agreement with experiments using translational energy spectroscopy.[5] Except for the total electron-capture cross sections, no agreement is found with the theoretical study—the explanation being that far too few states were included in the calculations.

It appears to be a general feature of charge-transfer processes that one must include a large number of strongly coupled states. It is necessary to describe all of these potential curves to an accuracy which is at least consistent over the whole relevant range of nuclear separation R. In particular, the splittings between the asymptotic states must be reproduced accurately; otherwise the regions of strongly avoided crossings, where the charge transfer actually occurs, are significantly displaced and the whole calculation is vitiated. The charge transfer is driven by the radial coupling matrix elements of the form

$\langle \Phi_1 | \partial/\partial R | \Phi_2 \rangle$ which are large in regions of avoided crossings. These integrals are most easily computed numerically using the finite-difference method. This imposes a requirement of a consistent amount of electron correlation in all the relevant states for all relevant values of R.

In this work we present preliminary results for the C^{3+}-H system. We address ourselves to the determination of potential energy curves that cover sufficient states, are of sufficient accuracy, and include a uniform amount of electron correlation. For this purpose we employ the spin-coupled valence-bond (VB) theory. In previous work, we have shown that this modern version of valence-bond theory is capable of describing—to a useful accuracy—not just ground states, or the lowest state of each symmetry, but several excited states of the same symmetry. Moreover, because of the non-orthogonality of the orbitals, the number of configurations needed is very small: about 200 spin-coupled configurations are sufficient for the system under study. Consequently, the theory possesses a high degree of visuality and the physical characteristics of the various interacting states are displayed. We confine ourselves to states of CH^{3+} of $^1\Sigma^+$ symmetry in this paper. Provided sufficient accuracy is achieved, we can contemplate the next stage of the problem. Further work, which includes the $^3\Sigma^+$ states, will be undertaken together with the determination of the radial coupling matrix elements.

In Sec. II, a brief description is provided of the spin-coupled VB calculations. The resulting potential energy curves are presented in Sec. III and are compared with previous calculations. Finally, the results are assessed and the outlook for further work is discussed.

II. SPIN-COUPLED VB CALCULATIONS OF STATES OF CH^{3+}

The spin-coupled wave function is of the form[6]

$$\Psi_{SM} \equiv \sum_k c_{Sk} \mathscr{A}(\phi_1 \phi_2 \phi_3 \phi_4 \Theta_{S,M,k}^4)$$

$$\equiv \{\phi_1 \phi_2 \phi_3 \phi_4\} . \tag{2.1}$$

The four orbitals ϕ_μ are taken to be of σ symmetry, and the total spin $S = 0$ so that Ψ_{SM} describes a state of $^1\Sigma^+$ symmetry. The sum over k is over all allowed spin couplings; in the present case of $N = 4$ and $S = 0$, this is just 2. The orbitals possess the following qualitative character:

$$\phi_1 \approx 1s(C) , \quad \phi_2 \approx 1s'(C) , \quad \phi_3 \approx 2s(C) , \quad \phi_4 \approx 2s'(C) ,$$

so that the ground state of the system corresponds, at long range, to $C^{2+}(2s^2) + H^+$.

Each orbital is expanded in a basis set of atom-centered functions χ_P:

$$\phi_\mu = \sum_P c_{\mu P} \chi_P . \tag{2.2}$$

For this purpose we use the universal even-tempered (UET) set which we have employed on a number of previous occasions.[7] This is a very large basis of Slater functions $(36\sigma, 18\pi_x, 18\pi_y, 6\delta_{xy}, 6\delta_{x^2-y^2})$ with exponents sys-

tematically generated as a geometric series. This basis is not biased towards any particular range of R, nor towards any particular state. On each center these are nine $1s$, six $2p$, and three $3d$ functions; the s and p spaces are fairly saturated and there are sufficient d functions to act as polarization functions, but we recognize that the basis may need some extension for the accurate description of atomic d orbitals. The basis includes several diffuse functions and, consequently, is well able to describe the large variety of states, including those with Rydberg character that one needs to take into account for CH^{3+}.

The orbital coefficients $c_{\mu P}$ occurring in (2.2), and the spin-coupling coefficients c_{Sk} shown in Eq. (2.1) are simultaneously optimized by means of a second-derivative procedure which we refer to as the "stabilized Newton-Raphson procedure." We find spin-coupling coefficients $c_{01} \approx 0$ and $c_{02} \approx 1$ for the whole range of R studied. This corresponds to the situation where the two carbon $1s$ orbitals remain coupled to singlet spin throughout. The overlap between the $1s(C)$ and $1s'(C)$ orbitals is large: it remains practically constant at 0.97, almost independent of R.

At convergence, for each occupied ϕ_μ we determine a set of excited-state or "virtual" orbitals $\phi_\mu^{(i)}$, $i = 1, 2, \ldots, m$. Each set is orthonormal, but is not orthogonal to the virtual orbitals derived from the other occupied orbitals:

$$\langle \phi_\mu^{(i)} | \phi_\nu^{(j)} \rangle = \begin{cases} \delta_{ij} & \text{if } \mu = \nu , \\ \Delta_{ij}^{\mu\nu} & \text{otherwise} . \end{cases} \tag{2.3}$$

Excited spin-coupled configurations are obtained by replacing one, two, or more occupied orbitals by these virtual orbitals. The total wave functions are in the form of a linear combination of the spin-coupled function (2.1) and the excited configurations:

$$\Psi_{SM} \equiv C_0 \{\phi_1 \phi_2 \phi_3 \phi_4\}$$

$$+ \sum_{i,j,k,l} C_{ijkl} \{\phi_1^{(i)} \phi_2^{(j)} \phi_3^{(k)} \phi_4^{(l)}\} . \tag{2.4}$$

The final energies of the various states and the corresponding eigenvectors are determined by forming the matrix of the Hamiltonian over the spin-coupled structures and diagonalizing.

The orbitals that were included in the final calculations are listed in Table I, together with their qualitative character for large nuclear separation (30.0 bohrs). Note that there is still considerable polarization at this distance. The calculations include 12σ and 16π orbitals; no orbitals of δ symmetry were used and no virtual orbitals from the stacks corresponding to $1s(C)$ or $1s'(C)$ were employed.

The form of the total wave functions (2.4) in which each occupied orbital ϕ_μ is replaced by a series of functions $\phi_\mu^{(i)}$ from its own stack ("vertical excitations") is equivalent to the expansion of the exact N-electron wave function in N distinct complete sets. Since each set $\{\phi_\mu^{(i)}\}$ is, in a certain sense, optimal for that particular electron coordinate, we may expect the expansion (2.4) to converge well. In the case of CH^{3+}, approximately 200 such spin-coupled configurations are sufficient to attain good convergence for the first ten states. Experience shows that

TABLE I. Virtual orbitals used in the final VB calculation and their character at large nuclear separation (30.0 bohrs). An orbital of σ symmetry which is the ith solution (ordered by energy) of stack μ is denoted as $S\mu i$. Similarly, a pair of π orbitals is denoted as $P\mu i$. The occupied orbitals are those in the first row.

$S\,1\,1$	$S\,2\,1$	$S\,3\,1$	$S\,4\,1$
C(1s)	C(1s)	C(2s + λ2p)	C(2s − λ2p)
		$S\,3\,2$	$S\,4\,2$
		C(2p − λ2s)	C(2p + λ2s)
		$S\,3\,3$	$S\,4\,3$
		C(3s + μ3p)	C(3s − μ3p)
		$S\,3\,4$	$S\,4\,4$
		H(1s)	H(1s)
		$S\,3\,5$	$S\,4\,5$
		C(3p − μ3s)	C(3p + μ3s)
		$P\,3\,1$	$P\,4\,1$
		C(2p)	C(2p)
		$P\,3\,2$	$P\,4\,2$
		C(3p + λ3d)	C(3p − λ3d)
		$P\,3\,3$	$P\,4\,3$
		C(3d − λ3p)	C(3d + λ3p)
		$P\,3\,4$	$P\,4\,4$
		H(2p)	H(2p)

the description of charge-transfer or ionic states is significantly improved by the addition of configurations in which two occupied orbitals are excited into the same virtual orbital, i.e., by relaxing, to some extent, our rule of "vertical excitations only."

Excited configurations were generated in the present case by all single and double replacements of occupied orbitals ϕ_3 and ϕ_4 by virtual orbitals. This gives rise to only 127 spatial configurations. When the two possible spin couplings are taken into account for those configurations containing no doubly occupied orbitals, this produces a total of 228 spin-coupled configurations.

III. DISCUSSION AND CONCLUSIONS

In Table II the computed splittings between the asymptotic states are compared with the experimental values for the first eleven states. The asymptotic energies have been computed at 30 bohrs and the energies of the $C^{2+}(nl,n'l')+H^+$ states have been corrected for the Coulombic repulsion at this distance. In general, it can be seen that the agreement is very good. The lowest nine potential energy curves are shown in Fig. 1; correspondence is invited from anyone requiring tables of the computed points.

The only disappointing asymptotic energy is for the $C^{2+}(2s\,3d\,;^1D)+H^+$ limit, which experimentally is almost exactly resonant with the $C^{3+}(2s)+H(1s)$ charge-transfer state. The virtual orbitals $S\,3\,6$ and $S\,4\,6$ (see Table I caption for explanation of notation) have $3d\sigma$

TABLE II. Asymptotic energies of the first eleven states of CH^{3+}. The experimental values are based on Moore's tables of atomic energy levels (Ref. 10). The calculated values are based on the values at 30 bohrs, but have been corrected for the Coulombic repulsion at the distance. The calculation described in the text did not produce the $C^{2+}(2p\,3p\,;^1P)$ limit. The energy quoted for this in the table comes from a slightly larger calculation, with 156 spatial configurations, which included the virtual orbitals $S\,3\,6$, $S\,4\,6$, $P\,3\,5$, and $P\,4\,5$. With the exception of the $C^{2+}(2s\,3d\,;^1D)$ level, which was improved (lowered) by 0.51 eV, there were only very small changes (<0.02 eV) for the other limits.

	Energy (eV)	
State	Experiment	Calculated
$C^{2+}(2s^2;^1S)+H^+$	0	0
$C^{2+}(2s\,2p;^1P)+H^+$	12.69	13.03
$C^{2+}(2p^2;^1D)+H^+$	18.08	18.54
$C^{2+}(2p^2;^1S)+H^+$	22.63	23.55
$C^{2+}(2s\,3s;^1S)+H^+$	30.65	30.69
$C^{2+}(2s\,3p;^1P)+H^+$	32.10	32.19
$C^{3+}(2s;^2S)+H(1s)$	34.27	34.29
$C^{2+}(2s\,3d;^1D)+H^+$	34.28	36.73
$C^{2+}(2p\,3s;^1P)+H^+$	38.44	39.13
$C^{2+}(2p\,3p;^1P)+H^+$	39.64	39.97
$C^{3+}(2p;^2P)+H(1s)$	42.28	42.34

character at large internuclear distance; inclusion of these in a slightly larger VB calculation improves the asymptote by 0.51 eV. Future improvements require modifications to the d space of our basis set, as we have already mentioned. In addition, $C^{2+}(2s\,3d\,;^1D)$ may be expected to interact strongly with $C^{2+}(2s\,4d\,;^1D)$ which lies about 5.9
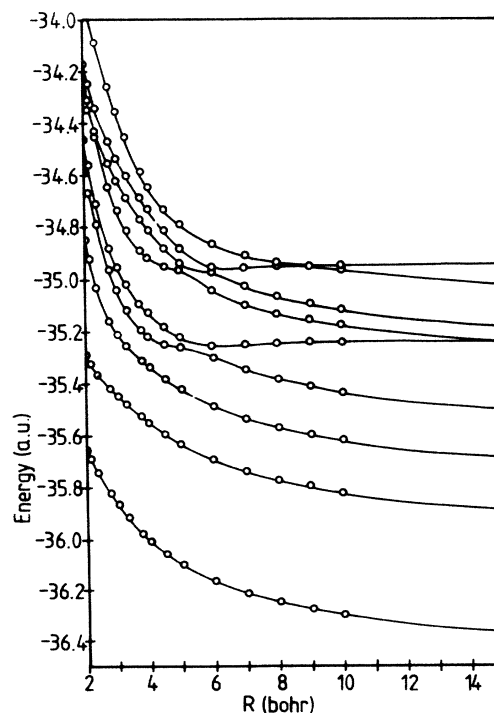

FIG. 1. Potential energy curves for the process $C^{3+}(2l)+H(1s)\rightarrow C^{2+}(nln'l';^1L)+H^+$. The nine lowest states of CH^{3+} of $^1\Sigma^+$ symmetry are shown.

eV higher in energy, there being a one-electron contribution to the relevant matrix element.

From Fig. 1 it is possible to trace diabatic paths for the $C^{3+}(2s)+H(1s)$ and $C^{3+}(2p)+H(1s)$ charge-transfer states. The bound nature of both of these states should be noted. Avoided crossings with repulsive C^{2+}-H^+ states leads to potential wells capable of supporting vibrational levels. For example, the computed potential for the $(5)^1\Sigma^+$ state shows a minimum near 6 bohrs at an energy of approximately 32 eV but, because of an avoided crossing near 15 bohrs with the $(6)^1\Sigma^+$ state, it dissociates adiabatically to the $C^{2+}(2s\,3s;^1S)+H^+$ limit some 1.3 eV lower. The potential maximum of the $(5)^1\Sigma^+$ state lies nearly 4000 cm^{-1} above the minimum and we can find eight vibrational levels beneath it. For the first few of these, the widths due to predissociation by tunneling through the barrier are negligible. Provided transition dipole moments to lower state are sufficiently large, it may be possible to detect photoemission from such levels.[8] The $C^{3+}(2s)+H(2l)$ limits lie at approximately 44.5 eV above the ground-state limit and are also likely to give rise to bound diabatic states.

In Fig. 2 we compare the present potential energy curves for for $C^{2+}(2p^2;^1S,^1D)+H^+$ and $C^{3+}(2s)+H(1s)$ with those used by Bienstock et al. in their quantal scattering study.[3] The potentials employed in their work were obtained using molecular-orbital configuration-interaction (MOCI) procedures.[9] Away from the avoided crossing region, the two sets of curves seem to be essentially parallel to one another, the spin-coupled VB calculation giving substantially lower energies for all nuclear separations and for all states. The largest discrepancies occur in the important region of the avoided crossing. This is seen to be far less sharp in the spin-coupled VB case, and the minimum energy separation is significantly greater than in the MOCI calculations. The computed cross sections for charge transfer depend sensitively on this separation and this may account at least partly for the lack of agreement between previous theory and the results from the photoemission experiments. The UET basis set used here, which is probably too large for MOCI calculations, should describe the $C^{2+}+H^+$ and $C^{3+}+H$ states to equal accuracy. The improvement over the MOCI calculations is substantially greater for one of the states, suggesting that the basis set used in the previous calculations may have been unbalanced.

The present calculations have shown that the ten lowest states of the CH^{3+} system, which are of highly contrasting character, can be determined to a useful accuracy in the spin-coupled VB framework by single and double excitations from the valence orbitals of a single reference function. The resulting total wave functions are very compact, and consist of a linear combination of just 228 spin-coupled configurations. The resulting potential ener-
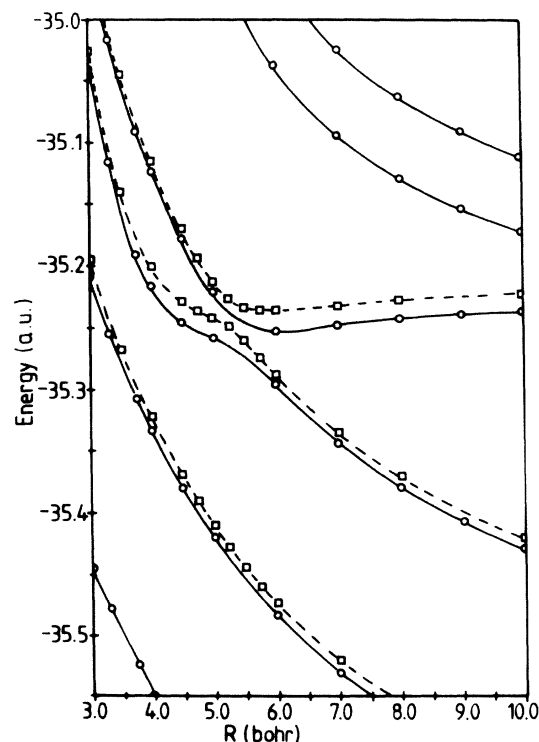

FIG. 2. Comparison of the present potential energy curves for $C^{2+}(2p^2;^1S,^1D)+H^+$ and for $C^{3+}(2s)+H(1s)$ with those used in the quantal scattering study of Bienstock et al. (Ref. 3). — ○ —, this work; — — □ — —, potentials used in Ref. 3.

gy curves represent a significant improvement over previous work. This is especially so in the crucial regions of avoided crossings. We do recognize a shortcoming in the present study for the $C^{3+}(2s\,3d;^1D)$ limit and we have noted how this may be rectified.

A complete description of charge transfer in the C^{3+}-H system requires the potential energy curves for $^3\Sigma^+$ symmetry, transition dipole moments between all the states, and the matrix elements of the radial coupling operator. From the experience gained here, it now appears very worthwhile to generate these quantities for CH^{3+} and, indeed, for other important systems. The final VB section of our programs is currently being modified in order to carry out the finite-difference procedure for computing the radial coupling elements. The compactness of the wave functions will be very advantageous here.

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