

Excited states of Na_2 dissociating into $3d + 3s$, $4p + 3s$, and $5s + 3s$

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All the excited adiabatic electronic states of Na_2 dissociating into $3d + 4s$, $4p + 3s$, and $5s + 3s$ atoms are calculated using a nonempirical pseudopotential, a flexible basis set, and the exact valence configuration-interaction treatment. Together with a highly precise work [G. H. Jeung, *J. Phys. B* **16**, 4289 (1983)], where all the electronic states dissociating into $3s + 3s$, $3p + 3s$, and $4s + 3s$ atoms have been calculated, this work reveals the lowest 38 electronic states of Na_2 . Wherever possible, the comparison of the present data with the recent spectroscopic observations shows excellent agreement. The majority of the theoretically predicted states remains to be found experimentally.

I. INTRODUCTION

The valence and the Rydberg states of the alkali-metal diatomic molecules have been stimulating subjects of study in spite of having the simplest possible molecular structure imaginable. In particular, a recent collection of the literature for Na_2 (Ref. 1) shows an impressive effort of both experimentalists and theoreticians working in this field for a century.

The current development in experimental spectroscopy using various laser sources and refined observation techniques gave a new enthusiasm in the resolution and the analysis of the highly excited states of diatomic molecules (for Na_2 , see Refs. 2–7). Consequently, the ever-increasing experimental data need to be classified and interpreted to get a comprehensive picture of the nature of highly excited states, to determine their roles in atomic and molecular collisions either chemically reactive or not, or to understand such phenomena as ionization or electron capture.

Theoretically, due to the recent development of the fast electronic computer with increasing size of the rapidly accessible memory devices and the simultaneous invention of many economical algorithms in numerical analysis, the lowest electronic states of alkali dimers, except Rb_2 , could be calculated with good precision.^{8–11}

In this paper, the excited states of Na_2 that lie higher than the currently known states are theoretically predicted. To do this, care is taken to give the best possible representation of the two valence electrons, keeping the core electrons almost the same all the way through. The calculational method and details will be explained in Sec. II. In Sec. III, the resulting adiabatic potential energies of the excited states will be reported and their nature will be discussed.

II. METHOD OF CALCULATION

There are three commonly used methods of calculation for alkali-metal diatomic molecules: (1) the all-electron frozen-core valence calculation, (2) the nonempirical pseudopotential valence calculation, and (3) the semiempirical (or model) pseudopotential valence calculation. In previ-

ous papers,^{10,12} the current problems in these methods are discussed and the core valence polarization and correlation (CV) terms lacking in the first and the second methods have been developed. The details of calculation using the nonempirical pseudopotential with the correction term are explained in a previous paper¹⁰ (referred to hereafter as I).

The main steps of calculation are as follows. Firstly, a basis set which can sufficiently well describe the $3s, 4s, 5s; 3p, 4p; 3d, 4d$ atomic states at the same time is determined in the atomic calculation. For the valence calculations, the pseudopotential parameters determined¹³ according to the Barthelat-Durand method¹⁴ and the CV energies according to Ref. 12 are used. The basis which consists in the Gaussian-type primitive functions [or orbitals (GTO's)] is reported in Table I. There the $3s, 4s, 5s; 3p, 4p; 3d, 4d$ atomic orbitals are also developed in terms of these GTO's. The absence of nodes for the $3s$ and $3p$ orbitals and the peculiar forms of their internal part are due to the nodeless pseudoorbitals inherent in the Barthelat-Durand method.

The calculated asymptotic molecular energies (sum of the two atomic energies) are compared to the experimental values (averaged over different J 's) in Table II. There it can be seen that the calculated valence energies which contain the CV term are in excellent agreement with the experimental ones. On the other hand, the energy levels of the $3d, 4p$, and $5s$ atomic states relative to the $4s$ state calculated without the CV correction term are in good agreement with the experimental values. The physical meaning of this point is that the correlation effect between the core electrons and the valence electrons disappears as the electron distribution becomes more and more diffuse. The slightly less good agreement of the $3d$ relative atomic energy can be found from the electron distribution of the $3d$ atomic orbital (AO) which has a non-negligible probability density near the core. One may infer from this, that as far as the molecular states which correlate with the $3d + 3s$ atomic states are concerned, the CV effect may be disregarded provided that the energies relative to the $4s + 3s$ (or higher) level are considered. To confirm this fact, the potential energy curves of the $3^1\Sigma_u^+$, $2^1\Pi_u$, $2^3\Pi_u$, $2^1\Pi_g$, and $2^3\Pi_g$ states calculated both with

TABLE I. Basis set used in this work and the atomic orbitals 3s, 4s, 5s; 3p, 4p; 3d, and 4d developed in this basis.

Types	Gaussian-type basis functions		Atomic orbitals			
	Exponents	Coefficients	n = 3	n = 4	n = 5	
s	2.836	0.007 043	1	0.31	-0.16	0.10
s	0.4932	-0.1871				
s	0.072 09	0.3679				
s	0.036 06	1				
s	0.016 67	1				
s	0.006 93	1				
s	0.002 87	1				
p	0.4310	-0.017 78	1	0.19	-0.13	0.77
p	0.092 76	0.2003				
p	0.035 62	1				
p	0.014 47	1				
p	0.005 80	1				
d	0.2920	0.014 54				
d	0.063 61	0.1230				
d	0.022 73	1	1	0.13	-0.10	-0.64
d	0.008 852	1				
d	0.003 52	1				
d						

and without the CV term are compared (see Fig. 1). As expected, the differential effect due to the CV term for these states is not very large in contrast to the lower-lying states dissociating into 3s + 3s and 3p + 3s where that effect is shown in previous works¹² to be non-negligible. Therefore, in this paper, in contrast to I, the CV correction is not included, while the basis set employed here is larger than that used in I.

The one- and two-electron integrals are calculated using the PSHONDO program.¹⁵ The valence electron energy is treated exactly through the complete configuration interaction (CI). The molecular orbitals (MO's) of Na₂⁺ are used as the basis functions for the valence CI. The adiabatic molecular potential energies are calculated for a wide internuclear distance interval of from 5 to 33 bohr.

The core-core interaction energy has been calculated considering two major contributions as in I: the frozen-core-frozen-core (in the atomic ground state) electrostatic repulsion, and the dipole-dipole dispersion term.

III. RESULT AND DISCUSSION

The calculated adiabatic energies as functions of the internuclear distance are tabulated in Table III and the potential curves are drawn in Fig. 2. All the states dissociating into the 3d + 3s, 4p + 3s, and 5s + 3s atomic separations are reported here. Together with I, this work includes 38 electronic states. Four Δ states dissociating into 3p + 3p are also calculated in this paper. The valence energy of 3s + 3s is -0.3777 hartree and the minimum ener-

TABLE II. Calculated valence energies and their differences versus the experimental ones: V (valence CI calculation), CV (core-valence correction). In -1×10^{-4} hartree.

Energy levels or differences	Valence Energies (-1×10^{-4} hartree)		
	Experimental ^a	V + CV ^b	V
3s + 3s	3777	3777	3644
3p + 3s	3003	3001	2918
4s + 3s	2604	2604	2525
3d + 3s	2447	2444	2379
4p + 3s	2397	2395	2326
5s + 3s	2264		2194
3s - 3p	0774	0776	0726
3p - 4s	0399	0397	0393
4s - 3d	0157	0160	0146
3d - 4p	0050	0049	0053
4p - 5s	0133		0132

^aFrom C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand. (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1971), Vol. 1.

^bFrom Ref. 10.

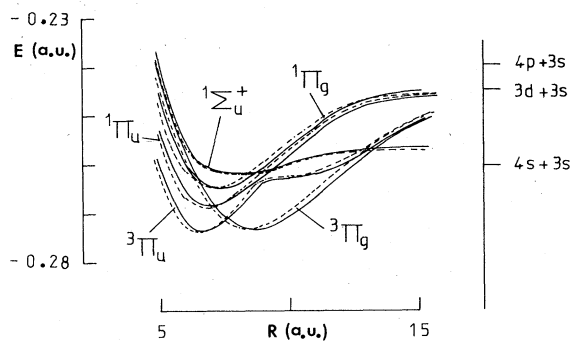


FIG. 1. Potential curves of the $3^1\Sigma_u^+$, $2^1\Pi_u$, $2^3\Pi_u$, $2^1\Pi_g$, and $2^3\Pi_g$ states calculated with (dashed curves) and without (solid curves) the core-valence correction term.

gy of the ground state $^1\Sigma_g^+$ is -0.4051 hartree. The dissociated atomic states corresponding to the different molecular states may be found by comparing the energy at infinity ($R = \infty$) to that of Table II.

The $^1\Sigma^+$ states show very complicated avoided crossing between different Rydberg and valence states at short internuclear distances, and also with ionic states (Na^+Na^-) at long internuclear distances. The first approximation of the ionic ground state through a simple $1/R$ term is also drawn in Figs. 2(a) and 2(b). This state subsequently crosses with the $2^1\Sigma_u^+$ and $3^3\Sigma_g^+$ states at energies between $3p+3s$ and $4s+3s$ at an internuclear distance of ~ 15 bohr, with the $3^1\Sigma_u^+$ and $4^1\Sigma_g^+$ states at higher energies (between $4s+3s$ and $3d+3s$) at longer distances (about 22 bohr), and then with the $4^1\Sigma_u^+$ and $5^1\Sigma_g^+$ states at still higher energies (near $3d+3s$) and at still longer distances (around 29 bohr). This curve crossing continues

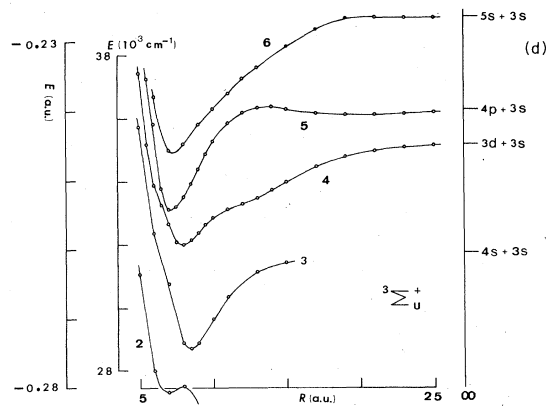
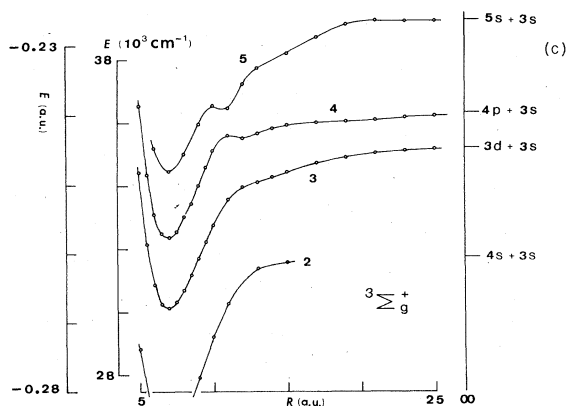
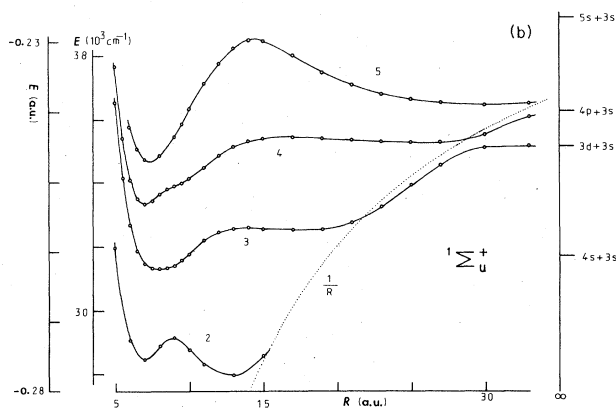
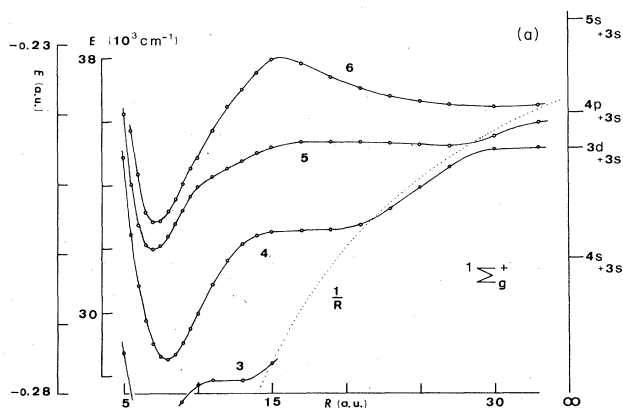


FIG. 2. Potential curves of the Σ^+ states (a)–(d), the Π states (e)–(g) and the Δ states (h) dissociating into the $4s+3s$, $3d+3s$, $4p+3s$, and $5s+3s$ atomic states. See the text for the (2) Δ states in (h).

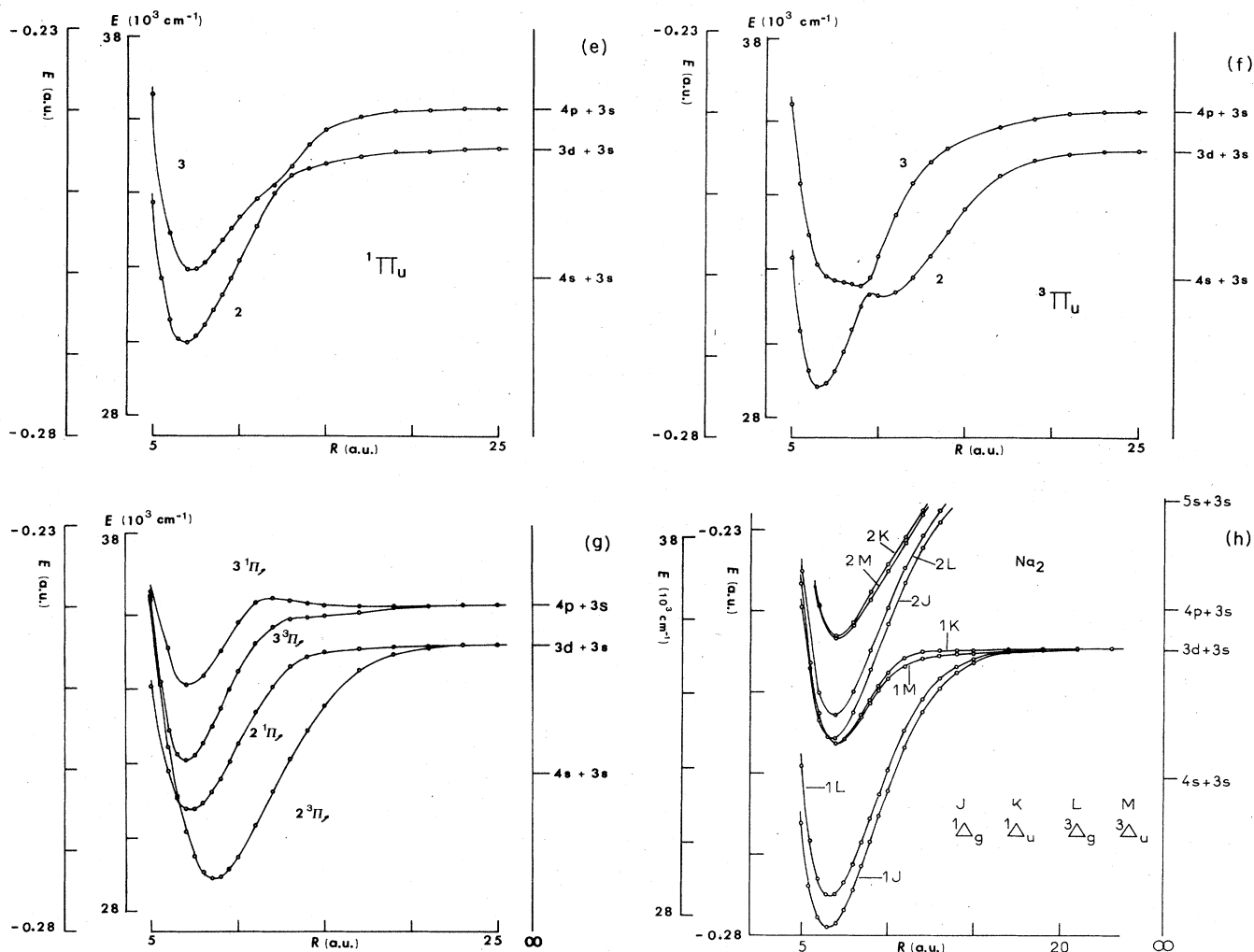


FIG. 2. (Continued).

at higher energies and larger internuclear distances. These successive crossings bring about a cascade of avoided crossings leading to either equilibrium wells situated at long internuclear distances (in the $2^1\Sigma_u^+$, the $4^1\Sigma_u^+$, and $5^1\Sigma_g^+$ states, and surely the $5^1\Sigma_u^+$ and $6^1\Sigma_g^+$ states) or steplike inflections (in the $3^1\Sigma_u^+$ state, the $3^1\Sigma_g^+$, and $4^1\Sigma_g^+$ states). Except for the $2^1\Sigma_u^+$ and $3^1\Sigma_g^+$ states, the $n^1\Sigma_u^+$ and $(n+1)^1\Sigma_g^+$ states are practically degenerate near the crossing points and beyond them, because at such distances the two electronic distributions centered at each atom hardly overlap.

The case of $2^1\Sigma_u^+$ has been recently analyzed simultaneously both in experiment^{16,17} and in calculation (I). There the inner well is essentially $4s+3s$ which has a significant orbital overlap at relatively short distances due to the diffuseness of the $4s$ orbital. The barrier between the inner and the outer wells is most probably a result of a strong interaction between the $4s+3s$ and the $3p+3s$ (compare the potential curves of $2^1\Sigma_u^+$ and $3^1\Sigma_u^+$). The outer well is the result of the crossing between the $3p+3s$ and the

ionic ground state (Na^+Na^-). The good quantitative agreement between the experimental analysis and I is to be noted.^{16,17} A similar double crossing occurs for the $3^1\Sigma_g^+$ and the $4^1\Sigma_g^+$ states, but does not give rise to a double-minima state.

A spectacular avoided crossing between $3p+3s$ and $4s+3s$ occurs in the triplet states, $2^3\Sigma_u^+$ and $3^3\Sigma_u^+$. The Σ^+ states lying over the $4s+3s$ asymptote show strong mutual interactions between different states of the same spin spatial symmetry resulting in many exotic potential curves. An evident crossing is shown in the $5^1\Sigma_u^+$ and the $6^1\Sigma_g^+$ states. The small splitting between the $4^3\Sigma_u^+$ and $5^3\Sigma_u^+$ states can also be noticed. To analyze the nature of these states will require either a nonadiabatic treatment or a valence-bond (VB) calculation as has been done previously.^{11,18} For example, to understand the strange shape of the $4^3\Sigma_g^+$, $5^3\Sigma_g^+$, and $6^3\Sigma_g^+$ states (not reported here) will require the use of partition schemes. In fact, for the states whose nature changes rapidly, a defined atomic configuration for the molecule has no meaning. This is

TABLE III. Calculated potential energies as functions of the internuclear distance for (a) Σ , (b) Π , and (c) Δ symmetry states. The energy unit is in -1×10^{-4} hartree.

(a)						
Potential Energies (1×10^{-4} hartree)						
R (bohr)	4	$^1\Sigma_g^+$ 5	6	3	$^1\Sigma_u^+$ 4	5
5	2462	2400		2387	2335	2253
5.5	2573	2501		2495	2437	
6	2646	2558	2497	2561	2495	2421
6.5	2696	2586		2598	2523	
7	2729	2594	2555	2616	2531	2467
7.5	2747	2589		2623	2527	
8	2751	2575	2539	2624	2517	2462
8.5	2743	2556		2623	2508	
9	2727	2536	2500	2620	2504	2435
9.5	2707	2517		2614	2500	
10	2685	2504	2460	2603	2494	2395
11	2643	2488	2427	2583	2478	2358
12	2609	2478	2393	2572	2461	2330
13	2586	2466	2365	2567	2448	2308
14	2573	2455	2340	2566	2441	2297
15	2568	2446	2322	2566	2437	2298
17	2566	2439	2327	2567	2436	2319
19	2565	2438	2347	2566	2437	2343
21	2557	2439	2363	2558	2439	2361
23	2534	2441	2374	2534	2441	2373
25	2504	2442	2381	2504	2442	2380
27	2475	2442	2385	2475	2442	2385
30	2449	2430	2388	2449	2430	2388
33	2446	2411	2386	2446	2405	2386
∞	2447	2397	2264	2447	2397	2264

R (bohr)	3	$^3\Sigma_g^+$ 4	5	4	$^3\Sigma_u^+$ 5	6
5	2482	2385	2287	2345	2257	
5.5	2587	2487		2448	2353	
6	2646	2544	2448	2506	2434	2379
6.5	2673	2571		2536	2511	
7	2679	2576	2481	2563	2541	2456
7.5	2671	2568		2589	2538	
8	2653	2546	2457	2592	2524	2447
8.5	2631	2528		2585	2504	
9	2607	2502	2413	2575	2483	2418
9.5	2582	2476		2564	2462	
10	2559	2450	2396	2554	2443	2395
11	2521	2428	2390	2541	2417	2374
12	2503	2434	2355	2533	2402	2352
13	2497	2426	2332	2524	2394	2336
14	2489	2419	2321	2513	2394	2321
15	2482	2414	2311	2501	2397	2308
17	2470	2410	2288	2479	2403	2282
19	2461	2408	2269	2466	2405	2266
21	2455	2406	2264	2457	2405	2264
23	2451	2404	2264	2452	2403	2265
25	2448	2401	2265	2449	2401	2265

TABLE III. (Continued).

R (bohr)	(b)							
	¹ Π _u		³ Π _u		¹ Π _g		³ Π _g	
	2	3	2	3	2	3	2	3
5	2513	2379	2578	2381	2498	2383		
5.5	2606	2486	2670	2488				
6	2657	2549	2718	2552	2602	2450	2573	2554
6.5	2681	2582	2738	2586	2635		2632	2582
7	2685	2595	2734	2602	2649	2496	2676	2589
7.5	2678	2594	2718	2607	2649		2707	2583
8	2664	2586	2695	2608	2641	2485	2726	2568
8.5	2646	2574	2667	2610	2627		2734	2548
9	2627	2559	2639	2613	2609	2454	2733	2525
9.5	2607	2545	2624	2603	2590		2723	2502
10	2586	2531	2625	2577	2569	2419	2709	2480
11	2543	2512	2621	2529	2529	2395	2670	2446
12	2501	2493	2604	2486	2496	2389	2628	2425
13	2479	2468	2576	2460	2474	2392	2588	2416
14	2470	2441	2546	2444	2462	2396	2552	2412
15	2464	2424	2518	2433	2456	2398	2521	2411
17	2456	2407	2477	2418	2452	2399	2479	2408
19	2451	2401	2458	2407	2449	2399	2459	2403
21	2449	2398	2450	2401	2448	2398	2451	2400
23	2447	2397	2448	2398	2447	2397	2448	2398
∞	2447	2397	2447	2397	2447	2397	2447	2397

R (bohr)	(c)							
	¹ Δ _g		³ Δ _g		¹ Δ _u		³ Δ _u	
	1	2	1	2	1	2	1	2
5	2661		2591		2367		2367	
5.5	2738		2683					
6	2779	2535	2731	2501	2527	2394	2528	2395
6.5	2791		2750					
7	2786	2557	2749	2528	2564	2431	2565	2434
7.5	2769		2735					
8	2744	2525	2712	2499	2546	2414	2548	2418
8.5	2715		2685					
9	2684	2473	2656	2449	2510	2377	2514	2386
9.5	2653		2626					
10	2622	2417	2597	2396	2477	2342	2484	2351
11	2568	2365	2547	2347	2457	2309	2467	2316
12	2525		2510		2450		2459	
13	2495		2484		2449		2455	
14	2475		2468		2448		2453	
15	2463		2458		2448		2452	
17	2452		2450		2447		2449	
19	2448		2447		2447		2448	
∞	2447	2230	2447	2203	2447	2203	2447	2230

especially true for short internuclear distances. No such analysis of the molecular states in terms of the atomic configurations is done in this work.

Apart from the crossing with the ionic states (Na⁺Na⁻) for the singlets, the long-distance behavior of the Σ⁺ states ($R \geq 17$ bohr) can be easily understood in terms of the orbital model. Namely, the energy difference between the *gerade* and *ungerade* states comes from the magnitude of the orbital overlap integral (S) between two AO's centered at each atom. The energy difference between the singlet and triplet comes from the exchange in-

tegral (K), the triplet being lower than the singlet for the pair dissociating into the same asymptotic states.

From the dissociation limit of the highest states presented in this paper, it seems likely that one (or more) of them may have $3p+3p$ characteristics. For example, the wave function of the highest ¹Σ_g⁺ and ³Σ_u⁺ states contain the $3p+3p$ components at short distances. The 12 electronic states which can be made with two $3p$ atoms are calculated using only p -type basis functions. This corresponds to the calculation of diabatic states. Among those states, the lower ¹Σ_g⁺ state, principally

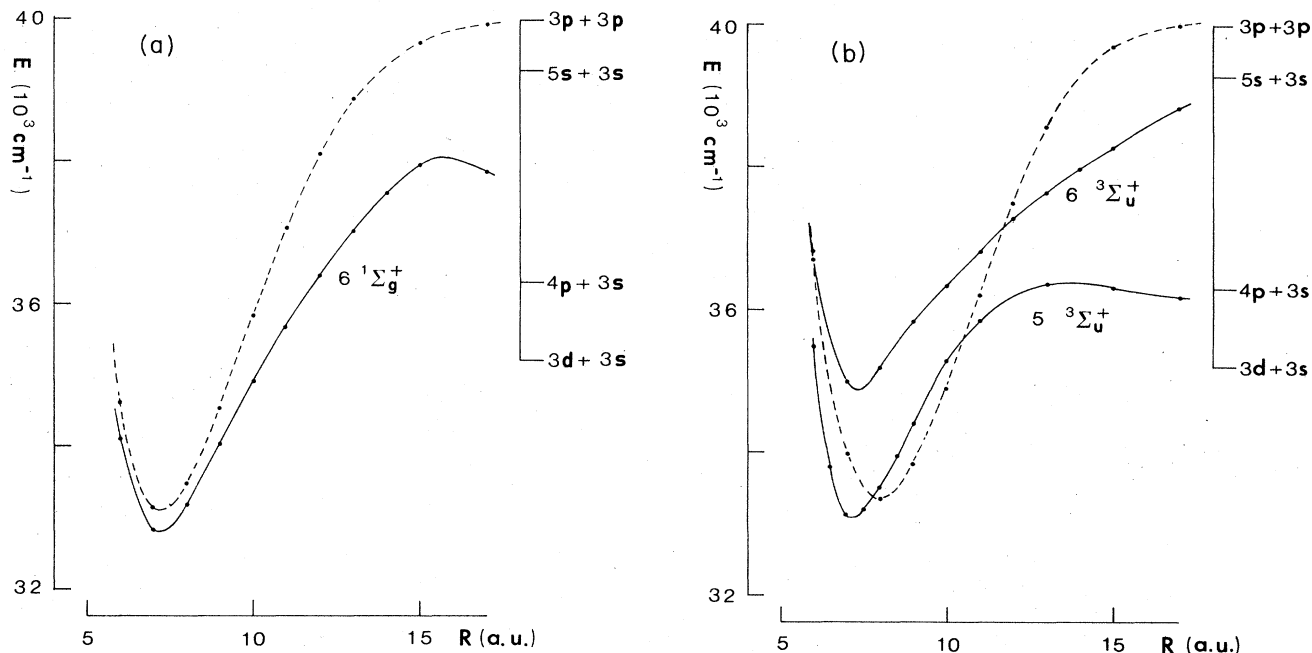


FIG. 3. Potential curves of diabatic $3p+3p$ states (dashed lines) compared with the potential curves of adiabatic states (solid lines) for the $1\Sigma_g^+$ symmetry (a), and the $3\Sigma_u^+$ symmetry (b).

$[\sigma_g(3p_\sigma-3p_\sigma)]^2$ and the lower $3\Sigma_u^+$ state, principally $\sigma_g(3p_\sigma-3p_\sigma) \times \sigma_u(3p_\sigma+3p_\sigma)$ are situated in the energy range of the adiabatic states dissociating up to $5s+3s$. These diabatic states are drawn in Fig. 3. The closeness of the $6^1\Sigma_g^+$ state to the diabatic $3p+3p$ state near the equilibrium point suggests that the former state is essentially $3p+3p$ in nature. For the $3\Sigma_u^+$ symmetry, the significant intermixing of the different atomic configurations leads to adiabatic states where the typical $3p+3p$ character is lost.

The Π states dissociating into $3d+3s$ and $4p+3s$ are drawn in Figs. 2(e)–2(g). The striking feature which can be seen at a first glance is that there are remarkable avoided crossings in the ungerade symmetries (between the 2 and $3^3\Pi_u$ states, and between the 2 and $3^1\Pi_u$ states), while this is not the case for the gerade symmetries.

To analyze the origin of these avoided crossings, diabatic $1\Pi_u$ and $3\Pi_u$ states have been calculated using three sets of basis functions: (i) s and d basis which will give diabatic states corresponding to $3d+3s$ atomic states, (ii) s and p basis which will give diabatic states corresponding to $4p+3s$ atomic states, and (iii) p -only basis which will give diabatic states corresponding to $3p+3p$ atomic states. The resulting potential energy curves of the diabatic states of $1\Pi_u$ symmetry and of $3\Pi_u$ symmetry are drawn in Fig. 4. The $1\Pi_u(3d+3s)$ and $1\Pi_u(4p+3s)$ states cross each other only once at about 13 bohr. The interaction of these two states makes the 2 and $3^1\Pi_u$ adiabatic states [compare Fig. 4(a) with Fig. 2(e)]. Energetically the $1^1\Pi_u$ state which is essentially $3p+3s$ is too low, and the $1\Pi_u(3p+3p)$ state is too high [not reported in Fig. 4(a)] to affect the 2 and $3^1\Pi_u$ states. In contrast, the $3\Pi_u(3d+3s)$ and $3\Pi_u(4p+3s)$ states cross each other at $R \approx 9.5$ bohr and again at 14.5 bohr. Between these dis-

tances their energies are very close. This leads to a larger splitting of the two adiabatic states 2 and $3^3\Pi_u$. The interaction Hamiltonian $\langle(3d+3s)|H|(4p+3s)\rangle$ for $3\Pi_u$ is greater than for $1\Pi_u$ for internuclear distances beyond 10 bohr. Here again the diagonal matrix element $\langle(3p+3s)|H|(3p+3s)\rangle$ and $\langle(3p+3p)|H|(3p+3p)\rangle$ are either too low (former) or too high (latter) to be efficiently involved in interaction with $3d+3s$ and $4p+3s$. The $2^3\Pi_u$ state closely resembles the $3\Pi_u(3d+3s)$ state for $6 \lesssim R \lesssim 9$. The $3d+3s$ state is lower than the $4p+3s$ state for the $3\Pi_u$ symmetry while the reverse is true for the $1\Pi_u$ symmetry.

In the Π_g symmetry states, the singly occupied π_g MO is antibonding between the two atoms. Due to the favorable directionality, the two $3d_\pi$ AO's can efficiently avoid each other by combining in phase and at the same time avoid the overlap with the singly occupied bonding MO σ_g , thus minimizing the Coulomb integral (J). The two $4p_\pi$ AO's are less well suited for this purpose. This may explain the noninterfering feature of the Π_g states. One may observe also the large separation at long distances between the singlets and the triplets dissociating into $3d+3s$, the triplets being lower than the singlets (compare the $2^3\Pi_u$ and $2^3\Pi_g$ with the $2^1\Pi_u$ and $2^1\Pi_g$). This is due to a large exchange integral K between the σ_g and $\pi(3d)$ MO's.

The Δ states in Fig. 2(h) have smooth curves, showing no apparent incidence of interaction. The gerade symmetry states are energetically much lower than their ungerade partners, which can be easily understood as the former have a singly occupied bonding δ_g MO apart from the singly occupied bonding σ_g MO while the latter have a singly occupied antibonding δ_u MO. The 2 Δ states reported in Fig. 2(h) have a singly occupied δ orbital of

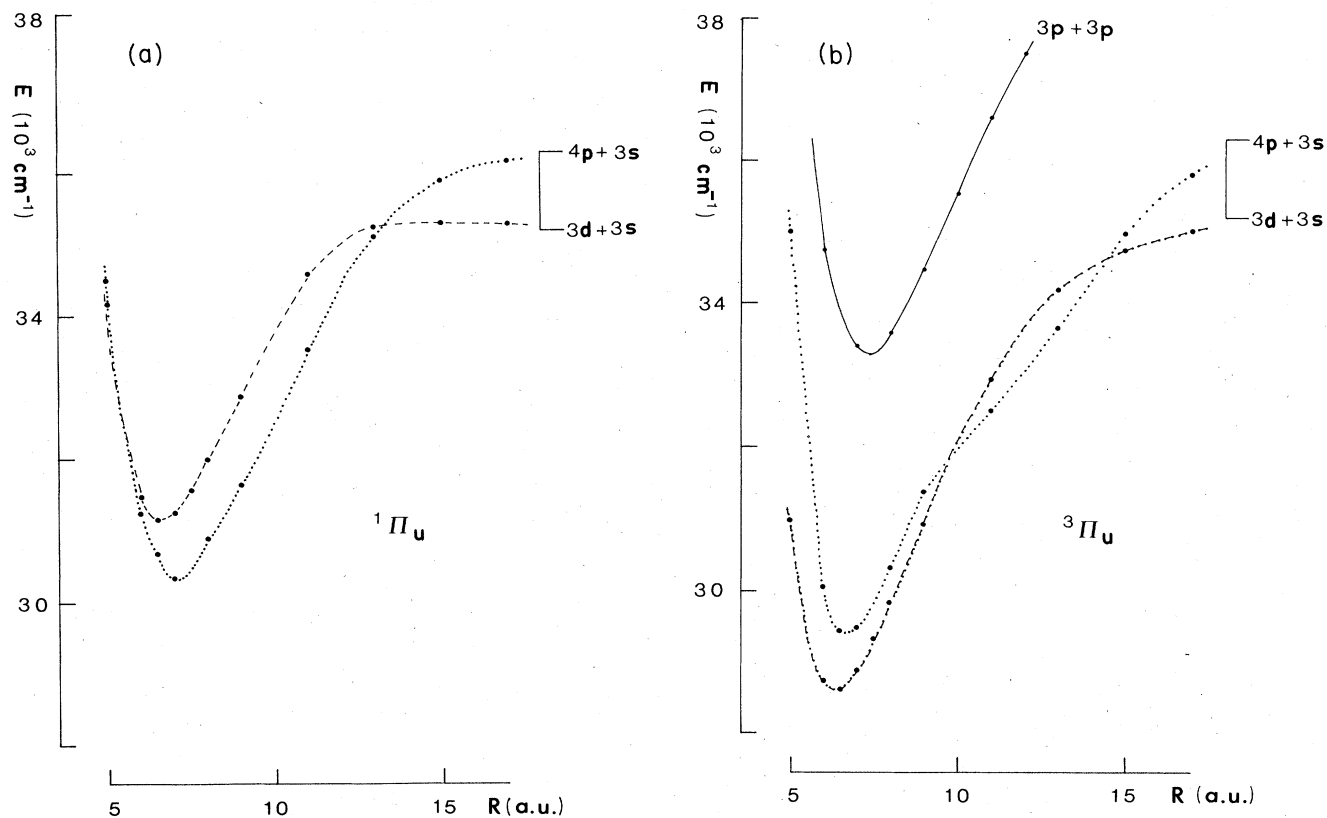


FIG. 4. Diabatic potential curves of the ${}^1\Pi_u$ (a) and ${}^3\Pi_u$ (b) symmetry states: the $3d+3s$ (dashed lines), the $4p+3s$ (dotted lines), and the $3p+3p$ (solid line) states.

mainly $4d$ character so they can be diabatically correlated to the $4d+3s$ separated atoms. As this asymptote is situated higher than the $3p+3p$ asymptote, these Δ states must have at least one avoided crossing with the Δ states coming from the $3p+3p$ atoms.

In Table IV are reported the calculated equilibrium characteristics. There are a few experimental data for the states calculated in this work. Spectroscopic data began to be available only recently due to the use of the optical resonance techniques. It may be seen that wherever the comparison is possible, the agreement between experiment and the present values is good. In particular, the present transition energies from the ground state ($X^1\Sigma_g^+$) differ by less than approximately 200 cm^{-1} with the experimental values. The calculated T_e values are systematically higher than the experimental ones: this may come from the incomplete basis set and small CV effect. The highest states of each spin spatial symmetry calculated here may suffer more from the poorness of the basis set for atomic states lying higher than $5s$. Specifically, the potential energies at short internuclear distances may be lacking in precision. The lowest ${}^1\Delta_g$ state observed by Carlson *et al.*³ designated as $5d\delta_g$ has a value $T_e = 34.9 \times 10^3\text{ cm}^{-1}$. This is higher than the calculated ${}^3{}^1\Delta_g$ state dissociating into $4d+3s$ (not reported here), where $T_e = 34.5 \times 10^5\text{ cm}^{-1}$.

Polarization labeling as employed by Schawlow *et al.*^{2,3}

can give the Λ values needed to identify the axial symmetry of the Rydberg states pumped by the optical resonance technique, but the analysis of the atomic configuration for these states cannot be made. The tentative designations in those works are not without ambiguity. For example, the attribution of the $4^1\Sigma_g^+$ states as $3p+3p$ (Ref. 2) seems incorrect according to the present calculation. The wave function of this state indicates rather $3d+3s$ near the equilibrium distance.

Most of the electronic states reported here already closely resemble the ground state of Na_2^+ near the equilibrium distances, this resemblance being better for the higher states. Namely, their ω_e and B_e values compare well to those of the $\text{Na}_2^+(X^2\Sigma_g^+)$: $\omega_e = 120.8 \pm 0.5\text{ cm}^{-1}$ and $B_e = 0.113 \pm 0.002\text{ cm}^{-1}$.⁵ The convergence of these values are either from the higher side or from the lower side according to the parity of the electronic wave function. This fact and the convergence rate may be well explained in the MO model as has been mentioned by Schawlow *et al.*^{2,3}

A recent analysis of the highly excited ($n > 15$) Rydberg states,¹⁹ in terms of the quantum defect theory, showed that the one Rydberg electron may be represented in a quasiatomic configuration such as $ns\Sigma^+$, $np\Sigma^+$, $np\Pi$, $nd\Sigma^+$, $nd\Pi$, and Δ , etc. In fact, the highly excited Rydberg states near the equilibrium internuclear distance of the ground state $\text{Na}_2(X^1\Sigma_g^+)$, which can be popu-

TABLE IV. Calculated equilibrium spectroscopic constants. In parentheses are the experimental values: 4, 5, and 6 $^1\Sigma_g^+$ from Ref. 2; 2 and 3 $^1\Pi_g$ from Ref. 3; 4 $^3\Sigma_g^+$ and 3 $^3\Pi_g$ from Ref. 7.

State	R_e (bohr)	T_e (10^3 cm $^{-1}$)	ω_e (cm $^{-1}$)	B_e (cm $^{-1}$)
4 $^1\Sigma_g^+$	7.91	28.5 (28.325 61)	107 (108.7384)	0.0838 (0.089 94)
5 $^1\Sigma_g^+$	7.01	31.9 (31.879 81)	110 (110.4895)	0.107 (0.109 32) (0.113 98)
6 $^1\Sigma_g^+$	7.18	32.8 (32.562 16)	119 (123.6736)	0.101 (0.105 86)
3 $^1\Sigma_u^+$	7.92	31.3	45	0.0836
4 $^1\Sigma_u^+$	7.01	33.3	108	0.107
5 $^1\Sigma_u^+$	7.21	34.7	93	0.101
3 $^3\Sigma_g^+$	6.92	30.1	117	0.109
4 $^3\Sigma_g^+$	6.93	32.3 (32.151)	114	0.109
5 $^3\Sigma_g^+$	6.8	34.4		0.114
4 $^3\Sigma_u^+$	7.84	32.0	106	0.0853
5 $^3\Sigma_u^+$	7.14	33.1	149	0.103
6 $^3\Sigma_u^+$	7.4	34.9		
2 $^1\Pi_g$	7.27	30.7 (30.582 73)	98 (102.579)	0.0992 (0.103 05)
3 $^1\Pi_g$	7.03	34.1 (33.810 66)	(107.590)	0.106 (0.104 26)
2 $^1\Pi_u$	6.90	30.0	108	0.110
3 $^1\Pi_u$	7.23	31.9	98	0.100
2 $^3\Pi_g$	8.66	28.9	92	0.0698
3 $^3\Pi_g$	6.99	32.1 (31.923 13)	113 (117.58)	0.107 (0.103 32)
2 $^3\Pi_u$	6.64	28.8	139	0.119
3 $^3\Pi_u$	9.0	31.5		0.0643
1 $^1\Delta_g$	6.58	27.6	125	0.121
2 $^1\Delta_g$	6.8	32.7		0.113
1 $^1\Delta_u$	7.02	32.6	108	0.106
2 $^1\Delta_u$	7.1	35.5		0.104
1 $^3\Delta_g$	6.71	28.5	124	0.116
2 $^3\Delta_g$	6.9	33.4		0.111
1 $^3\Delta_u$	7.04	32.6	107	0.106
2 $^3\Delta_u$	7.2	35.5		0.103

lated by optical resonance, may be considered as a united atom. For the highly excited states, the wave functions of the Rydberg electron may be developed without difficulty using the basis functions centered only at the midpoint between the two nuclei. But one should bear in mind that this fictitious united atom is very different from the single sodium atom (cf. Ref. 20). So the above mentioned ns , np , nd , etc. cannot be correlated with the AO's of Na. And for much longer internuclear distances where either the VB or the linear combination of AO-MO (LCAO-MO) model makes sense, a strong intermixing of the AO's (of isolated real atom) are unavoidable.

Recently, a semiempirical pseudopotential (or model potential) method has been used to calculate some of the electronic states reported here.²¹

IV. CONCLUDING REMARK

The 24 potential energy curves of the excited states of Na_2 dissociating into $3d+3s$, $4p+3s$, and $5s+3s$ atoms and the four Δ -state potential curves dissociating into $3p+3p$ and $4d+3s$ atoms are reported in the present paper, using the currently available nonempirical methods of calculation. These states already show a resemblance to the ground state of Na_2^+ , which indicates the diffuse nature of the second electron. The agreement between the equilibrium state spectroscopic constants given in this pa-

per and those available from experimental work to date is very good. This indicates that the LCAO-MO-CI method employed here (and implicitly the VB-CI method) works well for these electronic states. It seems also that for the other states dissociating into $3p+3p$ atoms, the present method gives quite good potential energies, as will be discussed in a later paper. It also appears probable that the atomic configuration analysis for the lowest 52 states up to $3p+3p$ makes sense and can be made for not too short internuclear distances when one uses either an appropriate diabatic framework or a VB treatment. The inclusion of the spin-orbit coupling may also be valuable as a supplementary instrument for this purpose.

To approach excited states still higher than those mentioned above we may need a very different method of calculation. The LCAO-MO-CI and VB-CI methods in their present state are not well adapted to dealing with the problems encountered in the calculation of highly excited states. On the one hand, the atomic energy levels above the $4d$ state are very dense, which requires so large a basis set to describe those atomic states at the same time that it becomes impossible to treat, even with only two valence electrons. On the other hand, if one tries to use a very diffuse atomic primitive function to describe those highly excited atomic states, one encounters a basis set linear dependence problem. That is, the two atomic basis func-

tions centered at the two nuclei are no longer distinguishable and a construction of the orthogonalized kets (either MO's or Slater determinants) is meaningless. The consequence will lack accuracy if it can be made at all, therefore the use of the AO's must be abandoned. These points need to be studied in detail to search for an alternative method of calculation. Besides, the success of the quantum defect theory for the highly excited Rydberg states of the alkali dimers which can be applied to short internuclear distances indicates the constant nature of the inner valence electron, and the near spherical symmetry description of the outer electron. This suggests that it may be

possible to give a simpler description of the molecular Rydberg states as a one-electron system with an effective Hamiltonian, at least for short internuclear distances.

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