[44] H. R. Griem (private communication).

[45] These authors generously provided us with the computer codes for executing the CO calculations.

[46] H. R. Griem, Comments At. Mol. Phys. 1, 27 (1969).

[47] B. Warner, Monthly Notices Roy. Astron. Soc. B9, 103 (1968).

[48] M. H. Miller and R. D. Bengtson, Astrophys. J. 156, 393 (1969).

[49] E. Shultz-Gulde, J. Quant. Spectry. Radiative Transfer 9, 13 (1969).

[50] C. E. Moore, Atomic Energy Levels, Natl. Bur. Std. (U.S.) Circ. No. 467 (U.S. Printing and Publishing Office, Washington, D.C., 1949).

[51] C. E. Moore, Natl. Bur. of Std. Reference Series No. NSRDS-NBS3, 1967, Part 2 (unpublished).

[52] W. C. Martin, J. Opt. Soc. Am. 49, 11, 1071 (1959).

[53] H. R. Griem, Eighth International Conference on the Phenomena in Ionized Gases, Vienna, 1967 (International Atomic Energy Agency, Austria, 1967).

[54] H. Van Regemorter, Astrophys. J. 136, 906 (1962).

[55] W. L. Wiese and A. W. Weiss, Phys. Rev. 175, 50 (1968).

PHYSICAL REVIEW A VOLUME 1, NUMBER 4 APRIL 1970

Bound States and Quasibound Resonances of Diatomic Systems*

W. E. Baylis†
Joint Institute for Laboratory Astrophysics, Boulder, Colorado 80302

(Received 8 September 1969)

The importance of quasibound resonances is emphasized, with special reference to alkali–noble-gas systems. A modified WKB method for calculating the distribution and properties of quasibound resonances as well as of bound states is reviewed and applied to calculations of KAr and RbAr ground states. The calculated distribution of states in a Lennard-Jones 6-10 potential agrees precisely with the exact results of Mahan and Lapp. Inclusion of quasibound resonances is found to increase the total number of states by about $\frac{2}{3}$. Tunneling lifetimes much larger than typical collisional destruction times are found for most resonances.

INTRODUCTION

Mahan and Lapp[1] have recently calculated the number of vibrational levels as a function of the rotational quantum number K for ground states of diatomic molecules composed of an alkali atom and a noble-gas atom. Their method is based on an exact solution of the Schrödinger equation valid only for a 6-10 Lennard-Jones potential when the total energy $E=0$. Consequently, it is useful only in calculating the number of bound states ($E<0$) of potential wells which can be adequately approximated by a 6-10 potential; energies of the states are not calculated. As Mahan and Lapp noted, their numbers are lower bounds on the numbers of effectively bound levels because quasibound resonances have not been included.

For many situations, quasibound resonances are as important as bound states. Such resonances, which have $E \geqslant 0$, may be contained by the "centrifugal barrier," $\hbar^2K(K+1)/2\mu R^2$, where $2\pi\hbar$ is Planck's constant, K is the rotational quantum number, μ is the reduced mass of the diatomic system, and R is the internuclear separation. Lifetimes as large as or larger than the collisional destruction time of the molecule are typical for alkali–noble-gas systems. Thus, for example, we expect resonances to be nearly as important as bound states in the elucidation of the satellite bands in line-broadened alkali spectra, the problem referred to by Mahan and Lapp.[1] Quasibound resonances are apparently also important in processes such as relaxation of optically oriented alkalis[2] and collisional-narrowing effects in alkali hyperfine transitions.[3] Indeed, whenever knowledge of the equilibrium density or the rate of formation of weakly bound molecules is of interest, it is a mistake to ignore quasibound resonances.[4]

An additional, possibly important property of quasibound resonances is that, in contrast to bound states, they can be formed during two-body collisions. The phenomenon is just that of long-lived "orbiting collisions," which have become of interest in recent years.[5] There are evidently some cases in which orbiting effects are observable even in thermally averaged total cross sections.[6]

There are various well-known methods for calculating bound-state energies for any potential – highly accurate numerical routines[7] for solving the radial Schrödinger equation as well as rapid, simple WKB methods.[8] Quasibound resonances have been treated by a modified WKB method in several papers on semiclassical scattering theory[9]; resonances may of course also be treated by more exact numerical methods.[5b] Because of its simplicity and the unified treatment available for both bound states and quasibound resonances, we use the WKB technique. In the following, we briefly review the method and then apply it to calculations of KAr and RbAr. Mahan and Lapp's results for KAr are used as a check on accuracy.

METHOD

The application of WKB[10] techniques to the study of bound[8] and quasibound states[9] is well known. Far below the top of the barrier, the unmodified WKB approximation is satisfactory; near the top, modifications – and, in particular, new "connection formulas" – are obtained by assuming the barrier there to be parabolic and by then solving the resulting Schrödinger equation exactly.[9] We shall now briefly review the germane equations thus obtained.

A diatomic system of reduced mass μ interacting via the internuclear potential $V(R)$ obeys the following radial equation:

$$\left(-\frac{\hbar^2}{2\mu}\frac{d^2}{dR^2}+U_K(R)-E\right)\mathcal{R}_K(R)=0\ , \tag{1}$$

where E is the total energy, K the rotational quantum number, $\mathcal{R}_K$ the radial wave function, and $U_K(R)$ the effective potential:

$$U_K(R)=V(R)+\frac{\hbar^2K(K+1)}{2\mu R^2}\quad . \tag{2}$$

The potential $V(R)$ is assumed strongly repulsive ($V \gg E$) near the origin, vanishingly small at large R, and attractive ($V<0$) over some intermediate range of R. Within the WKB approximation, we can calculate the bound states and quasibound resonances for virtually any such smoothly varying potential V. In the following, we restrict our attention to potentials $V(R)$ with only one minimum, though it is not difficult to extend the treatment to potentials with several minima.[9a]

Equation (1) represents a particle of mass μ and energy E moving in a one-dimensional potential $U_K(R)$. For quasibound resonances there will be three classical turning points $r_0<r_1<r_2$. For bound states, $r_2\to\infty$. In the classically allowed regions $r_0<R<r_1$ and $R>r_2$, we put

$$\hbar k\equiv\{2\mu[E-U_K(R)]\}^{1/2}\quad , \tag{3}$$

and in the forbidden regions $R<r_0$ and $r_1<R<r_2$,

$$\hbar\kappa\equiv\{-2\mu[E-U_K(R)]\}^{1/2}\quad . \tag{4}$$

We further define the phase integrals:

$$\beta(E)\equiv\int_{r_0}^{r_1}dRk\quad , \tag{5}$$

$$\gamma(E)\equiv\int_{r_1}^{r_2}dR\kappa\ . \tag{6}$$

Now $\hbar\, d\beta/dE$ is precisely t_{TR}, the classical one-way transit time for a particle in the well, and $\theta(E)\equiv\exp\gamma$ is a measure of the barrier opacity at energy E.

Using the WKB connection formula,[11] one can obtain the ratio of the particle amplitude inside the well ($r_0<R<r_1$) to that outside ($R>r_2$). The condition for a resonance is simply that this ratio be a maximum. One thereby finds the semiclassical condition for a bound or nearly bound state:

$$\beta(E_v)=\pi(v+\tfrac{1}{2}),\ v=0,1,2,\ldots,\quad . \tag{7}$$

At energies near E_b, the top barrier, the WKB approximation relating wave-function amplitudes on either side of the barrier becomes inaccurate. We may however approximate the effective potential near the top of the barrier by expanding $U_K(R)$ in a Taylor series about $R=R_0$, the position of the top of the barrier, and retaining terms only through $(R-R_0)^2$. The resulting radial wave equation can be solved exactly and the wave functions expressed in terms of parabolic cylinder functions[12] of complex index. Relating the asymptotic forms of the wave function to the WKB solutions on either side of the barrier allows us again to calculate the ratio of the particle amplitude inside and outside the well. The condition is then found to be[13]

$$\beta(E_v)=\pi(v+\tfrac{1}{2})-\tfrac{1}{2}\delta-\tfrac{1}{2}\arctan\left(\frac{1-\frac{1}{2}T-S}{1/\xi+\xi S(1-\frac{1}{2}T)}\right)\ , \tag{8a}$$

$$\simeq\pi(v+\tfrac{1}{2})-\tfrac{1}{2}\delta-\xi(2\theta)^{-4}+O(\theta^{-6})\quad , \tag{8b}$$

where $O(\theta^{-6})$ means "terms of order θ^{-6}."

In Eqs. (8), $\delta=\arg\Gamma(\frac{1}{2}+i\gamma/\pi)-(\gamma/\pi)\ln(\gamma\pi/e)$,a small non-negative phase angle which is zero when $\gamma=0$, has a maximum of 0.15 rad at $\gamma=0.18\pi$, and approaches zero again as θ becomes large[14]; $\xi=|d\gamma/dE|[d\beta/dE+\frac{1}{2}(d\delta/d\gamma)(d\gamma/dE)]^{-1}$; and $S[(1-T)/(1+\xi^2T^2/4)]^{1/2}$, where T is the barrier transmission coefficient given by the WKB method (the expression is exact for the case of a parabolic barrier[15]):

$$T(E)=(1+\theta^2)^{-1}\quad . \tag{9}$$

The corresponding semiclassical tunneling lifetime for a particle in the well is simply

$$\tau=2t_{\mathrm{TR}}/T\quad . \tag{10}$$

In summary, the method is as follows: The number of bound or quasibound vibrational states of energy $\leq E < E_b$ for a given rotational number K is the largest integer N_K satisfying

$$N_K \leq \frac{1}{2} + \frac{\beta(E)}{\pi} + \frac{\delta}{2\pi} + \frac{1}{2\pi}\arctan\frac{1-\frac{1}{2}T-S}{1/\xi+\xi S(1-\frac{1}{2}T)} \quad . \qquad (11)$$

The approximation of setting the arctan and $\delta/2\pi$ terms equal to zero is in most cases a good one; only when $E \approx E_b$ and $N_K + 1 < \beta(E)/\pi + \frac{3}{4}$ could the short-lived resonance thus be neglected. The energy of the N_Kth vibrational level is obtained by solving Eq. (11) for the energy E for which the equality holds. The transmission coefficient is given by Eq. (9), the lifetime, by Eq. (10).

RESULTS

The method described above is of course approximate, and even though the underlying WKB approximation has proved its value in a large variety of applications,[16] it is nevertheless valuable to have the exact calculations of Mahan and Lapp[1] with which to check it.

From a list of the number of vibrational levels $N_K(E)$ of energy $\leq E$ for each K, it is trivial to determine $K_{\max}(E,v)$, the maximum rotational quantum number for a given vibrational number v. In Table I, $K_{\max}(E,v)$ is given for the 6-10 potential used by Mahan and Lapp[1] for the KAr system. Values of $K_{\max}(0,v)$, which include only bound states, agree exactly with those of Mahan and Lapp. The values of $K_{\max}(E_b,v)$, which include also quasibound resonances, are about $\frac{1}{3}$ larger.

TABLE I. Bound states and quasibound resonances in a Lennard-Jones 6-10 potential with well depth $\epsilon = 50.345$ K $(\doteq 10^{-14}$ ergs) and equilibrium position $R_e = 8.126$ bohrs for a diatomic system of reduced mass $\mu = 19.760$ amu (C^{12}) which is the reduced mass for KAr.

v	$K_{\max}(0,v)^{a}$	$K_{\max}(0,v)^{b}$	$K_{\max}(E_b,v)^{b}$
0	31	31	41
1	27	27	35
2	23	23	29
3	19	19	24
4	15	15	19
5	11	11	14
6	7	7	9
7	3	3	4
$\frac{N_{\text{total}}(0)}{2S+1} =$	3264	3264	...
$\frac{N_{\text{total}}(E_b)}{2S+1} =$	...	...	5335

[a] Calculation of Mahan and Lapp (Ref. 1).

[b] Present calculations.

TABLE II. Bound states and quasibound resonances for the $X^2\Sigma$ state of RbAr. The potential is given numerically (see Ref. 19); it has a well depth $\epsilon = 43.524$ K and an equilibrium separation $R_e = 9.889$ bohrs.

v	$K_{\max}(0,v)$	$K_{\max}(E_b,v)$
0	43	57
1	39	52
2	36	46
3	32	41
4	28	36
5	24	31
6	20	26
7	16	20
8	12	15
9	7	7
$\frac{N_{\text{total}}(0)}{2S+1} =$	8423	
$\frac{N_{\text{total}}(E_b)}{2S+1} =$		14029

The total number of states $N_{\text{total}}(E)$ with energies $\leq E$ is readily obtained from the $K_{\max}(E,v)$. Recalling that each state has a rotational degeneracy of $2K+1$ and a spin degeneracy $2S+1$, we find

$$N_{\text{total}}(E) = (2S+1)\sum_{v}\sum_{K=0}^{K_{\max}(E,v)}(2K+1) = (2S+1)\sum_{v}[K_{\max}(E,v)+1]^2 \quad . \qquad (12)$$

We see that in Tables I and II, $N_{\text{total}}(E_b)$ exceeds $N_{\text{total}}(0)$ by about $\frac{2}{3}$.

Note that if one is only interested in $N_{\text{total}}(0)$, a very simple way to obtain it with an accuracy approaching that of the above-described WKB method when N_{total} is large is to sum over phase-space cells:

$$N_{\text{total}}(0) = (2S+1)\int d^3R \int_{V<E<0} d^3k\,(2\pi)^{-3} = \frac{2}{3\pi}(2S+1)\int_{V<0} dR\,R^2\left(-\frac{2\mu}{\hbar^2}V(R)\right)^{3/2} . \qquad (13)$$

For a Lennard-Jones (m,n) potential of well depth ϵ and equilibrium separation R_e, namely,

$$V(R)=\frac{\epsilon}{n-m}\left[m\left(\frac{R}{R_e}\right)^{-n}-n\left(\frac{R}{R_e}\right)^{-m}\right] \;, \quad (14)$$

$N_{\text{total}}(0)$ [Eq. (13)] reduces to[17]

$$N_{\text{total}}(0)=(2S+1)(2\mu\epsilon R_e^2/\hbar^2)^{3/2}\Phi(m,n) \;, \quad (15)$$

where $\Phi(m,n)$ is a number given by

$$\Phi=\frac{2}{3\pi}n^{-1}(1-m/n)^{-5/2}(n/m)^q B(q,\tfrac{5}{2}) \;, \quad (16)$$

with $q=3(\frac{1}{2}m-1)/(n-m)$. Here, $B(q,\frac{5}{2})$ is the β function[18]

$$B(q,\tfrac{5}{2})=\int_0^1 dx\, x^{q-1}(1-x)^{3/2}=\frac{\Gamma(q)\Gamma(\frac{5}{2})}{\Gamma(q+\frac{5}{2})} \;. \quad (17)$$

One finds, for example, that

$$\Phi(6,8)=\frac{2}{35\pi}(\tfrac{4}{3})^6=0.10220 \;, \quad (18a)$$

$$\Phi(6,9)=0.09451 \;, \quad (18b)$$

$$\Phi(6,10)=\frac{2}{3}\left(\frac{5}{4\sqrt{6}}\right)^3=0.08858 \;, \quad (18c)$$

$$\Phi(6,11)=0.08378 \;, \quad (18d)$$

$$\Phi(6,12)=0.07970 \;, \quad (18e)$$

$$\Phi(6,13)=0.07605 \;, \quad (18f)$$

$$\Phi(6,14)=0.07271 \;. \quad (18g)$$

TABLE III. Energies E of the bound and quasibound states of the $X^2\Sigma$ state of RbAr and barrier transmission coefficients T and tunneling lifetimes τ of the quasibound resonances. The interatomic potential used is the numerical calculation of Ref. 19.

K	v	E(K)[a]	T	τ (sec)
30	0	-19.506	0	bound
30	1	-12.942	0	bound
30	2	-7.235	0	bound
30	3	-2.479	0	bound
30	4	1.213	1.14×10^{-16}	$9.40\times10^{+4}$
30	5	3.621	6.46×10^{-2}	3.25×10^{-10}
40	0	-5.144	0	bound
40	1	0.497	$<10^{-50}$	$>10^{40}$
40	2	5.070	5.48×10^{-11}	1.53×10^{-1}
40	3	8.314	4.67×10^{-2}	3.01×10^{-10}

[a] For comparison, the barrier maximum is 3.951 K when $K=30$ and 8.930 K when $K=40$.

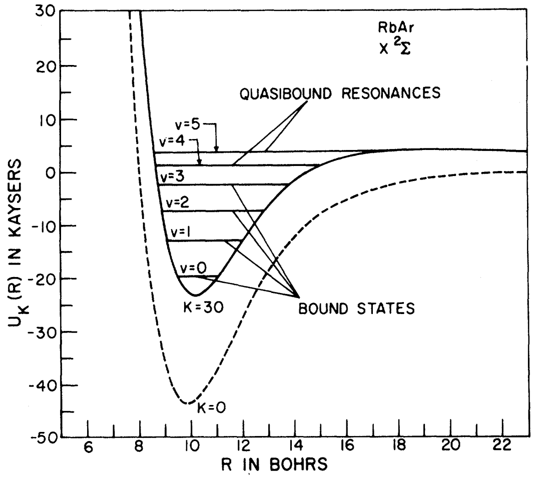

FIG. 1. Effective interatomic potential $U_K(R)$ [$=V(R)+\hbar^2K(K+1)/2\mu R^2$] of the $X^2\Sigma$ state of RbAr for $K=30$. Energies of the vibrational bound and quasibound states are shown. The dashed curve is the interatomic potential $V(R)$ (Ref. 19).

For the 6-10 KAr potential mentioned above, $N_{\text{total}}(0)$ as calculated by Eqs. (15) and (18c) is $3193(2S+1)$, in reasonable agreement with values obtained by summing over K values and given in Table I.

As emphasized above, an important feature of the WKB method described is that it can be used with a large variety of potential shapes. In Table II, we give values of $K_{\max}(0,v)$ and $K_{\max}(E_b,v)$ for a potential given only numerically. The potential is one calculated previously[19] by the author for the $X^2\Sigma$ (ground) state of RbAr; its well depth is $\epsilon=43.524$ K; its equilibrium position is $R_e=9.889$ bohrs; and it contains more phase space than the 6-10 potential of the same ϵ and R_e.

In Table III, energies of the RbAr bound states and quasibound resonances and tunneling lifetimes of the resonances are given for $K=30$ and $K=40$. The effective potential $U_K(R)$ and the bound and quasibound vibrational states are shown in Fig. 1 for $K=30$. Because ground-state well depths of alkali–noble-gas diatomics are small compared with normal thermal energies (for example, the binding energy of RbAr is about $\frac{1}{5}$ of room-temperature thermal energies),[19] we expect the cross section for collisional dissociation, i.e., for the process

$$\text{RbAr}+\text{Ar}\rightarrow\text{Rb}+2\text{Ar}$$

to be large, say, $\sigma\sim10^{-14}$ cm^2. Collisional-dissociation lifetimes τ_c will be correspondingly short. At noble-gas pressures of 100 Torr and room temperature, τ_c will be roughly the same as the shortest tunneling lifetimes listed in Table III, namely, about 3×10^{-10} sec. Consequently, even the highest of the quasibound resonances may in some situations be as important as the bound states.[20]

One property of quasibound resonances mentioned in the Introduction is that they can be formed during two-body collisions. The probability for such long-lived "orbiting collisions" is greatest for high-lying resonances, which have relatively large widths $\Gamma \simeq \hbar/\tau$ as well as relatively large barrier transmission coefficients T. For the highest levels listed in Table III, if the collision energy lies within $\frac{1}{2}\Gamma$ of the resonance energy at the given K, the probability is about 5% that an orbiting collision will occur.

ACKNOWLEDGMENTS

With thanks, I acknowledge helpful discussions with Dr. P. L. Bender and Dr. R. N. Zare.

---

[*] Work supported by National Science Foundation, under Grant No. GP-8052.

[†] Present address: Department of Physics, University of Windsor, Windsor 11, Ont., Can.

[1] G. D. Mahan and M. Lapp, Phys. Rev. 179, 19 (1969).

[2] M. A. Bouchiat, J. Brossel, and L. Pottier, Phys. Rev. Letters 19, 817 (1967); C. C. Bouchiat, M. A. Bouchiat, and L. C. L. Pottier, Phys. Rev. 181, 144 (1969).

[3] P. L. Bender and V. W. Cohen, in Abstracts of Papers to the Sixth International Conference on the Physics of Electronic and Atomic Collisions (MIT Press, Cambridge, Mass., 1969), p. 720.

[4] The significance of quasibound resonances for the virial coefficients and transport properties of gases was recognized by D. E. Stogryn and J. O. Hirschfelder, J. Chem. Phys. 31, 1531 (1959); 31, 1545 (1959); 33, 942 (1960).

[5] (a) W. C. Stwalley, in Abstracts of Papers to the Sixth International Conference on the Physics of Electronic and Atomic Collisions (MIT Press, Cambridge, Mass., 1969), p. 51 and references therein; (b) T. G. Waech and R. B. Bernstein, J. Chem. Phys. 46, 4905 (1967).

[6] R. H. G. Ried and A. Dalgarno, Phys. Rev. Letters 22, 1029 (1969).

[7] J. W. Cooley, Math. Comput. 15, 363 (1961); J. K. Cashion, J. Chem. Phys. 39, 1872 (1963); and R. N. Zare and J. K. Cashion, University of California Laboratory Report No. UCRL-10881, 1963 (unpublished).

[8] See, for example, G. M. Leies, J. Chem. Phys. 37, 1418 (1962); C. L. Beckel, *ibid.* 39, 90 (1963); E. J. Finn, *ibid.* 39, 2423 (1963). Second- and higher-order WKB approximations have also been used. See, for example, J. L. Dunham, Phys. Rev. 41, 721 (1932); H. Harrison and R. B. Bernstein, J. Chem. Phys. 38, 2135 (1963); C. L. Beckel, J. Nakhleh, and U. R. Chowdary, *ibid.* 40, 139 (1964); J. B. Krieger, M. L. Lewis, and C. Rosenzweig, *ibid.* 47, 2942 (1967); J. K. Cashion, *ibid.* 48, 94 (1968).

[9] (a) K. W. Ford, D. L. Hill, M. Wakano, and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 239 (1959) derive expressions for the scattering phase shift for energies both near the top of the barrier and well below the top. (The implication of their Fig. 2, namely, that the semiclassical condition for a bound state is applicable to resonances near the barrier top, is incorrect; however, their later treatment of the resonance condition is satisfactory.) Applications to problems in semiclassical scattering theory are made by K. W. Ford and J. A. Wheeler, Ann. Phys. (N.Y.) 7, 259 and 287 (1959). See also (b) R. R. Herm, J. Chem. Phys. 47, 4290 (1967); (c) W. H. Miller, *ibid.* 48, 1651 (1968). See also Ref. 4.

[10] N. Fröman and P. O. Fröman, JWKB Approximation (North-Holland Publishing Co., Amsterdam, 1965), and references therein.

[11] Reference 10, p. 86. As Fröman and Fröman emphasize, the authors of some standard texts on quantum mechanics have applied the WKB connection formulas without proper care for their directionality and, in some cases, have thus derived inaccurate results. See pp. 7, 51, and 97.

[12] See for example W. Magnus and F. Oberhettinger, Formulas and Theorems for the Functions of Mathematical Physics (Chelsea Publishing Co., New York, 1954), p. 91.

[13] Ford, Hill, Wakano, and Wheeler (Ref. 9) derive an expression for the resonance condition which is equivalent to Eq. (8) with the arctan term $=0$. Examination of their derivation reveals that they have neglected changes in the barrier opacity, i.e., they have effectively taken $d\gamma/dE = 0$. Note that for $\gamma > 0.18\pi$, the resonant values of β, and hence of E, near the barrier top are always shifted down slightly from the values predicted by Eq. (7).

[14] δ is exactly twice Miller's function $Q(\theta)$; see Ref. 9c, Eq. (6a).

[15] Reference 10, p. 94.

[16] In the Rydberg-Klein-Rees (RKR) method, for example, application of the WKB method is made to a related problem, namely, that of determining potential curves from spectroscopic constants. See, for example, J. T. Vanderslice, E. A. Mason, W. G. Maisch, and E. R. Lippincott, J. Mol. Spectry. 3, 17 (1959); 5, 83 (1960); R. H. Davies and J. T. Vanderslice, J. Chem. Phys. 45, 95 (1966). See also Ref. 8.

[17] Note that $N_{\text{total}}(0)$ depends on the $\frac{3}{2}$ power of the well "strength" $2\mu\epsilon R_e^2/\hbar^2$. This is as predicted generally by B. Simon, J. Math. Phys. 10, 1123 (1969). Cashion (Ref. 8) finds N_{total} proportional to the first power of the strength, but he does not include rotational degeneracy in his definition of N_{total}.

[18] See, for example, Ref. 12, p. 4.

[19] W. E. Baylis, J. Chem. Phys. 51, 2665 (1969).

[20] Stogryn and Hirschfelder found similar results for Ar_2 molecules: Except at quite low temperatures and pressures, where collision rates are low, most quasibound resonances may be treated as bound states. See Ref. 4.

PHYSICAL REVIEW A VOLUME 1, NUMBER 4 APRIL 1970

Hyperfine Structure of Sodium†

T. Lee, N. C. Dutta, and T. P. Das
Department of Physics, University of California, Riverside, California 92502*

(Received 15 August 1969)

The Brueckner-Goldstone many-body perturbation theory has been applied in a calculation of hyperfine structure (hfs) of sodium in the ground ($^2S_{1/2}$) state. Our result for A (as in $A\vec{I}\cdot\vec{J}$) is 857.8001 ±6 Mc/sec, in good agreement with the experimental result of 885.8131 ±0.0001 Mc/sec. The major contributions beyond the restricted Hartree-Fock result of 622.6430 Mc/sec arise from diagrams describing the exchange core-polarization effect. This contributes 139.6665 Mc/sec, in agreement with the existing unrestricted Hartree-Fock (UHF) and moment-perturbation (MP) results. All diagrams involving two orders of correlation interactions and associated ladders were calculated and were found to contribute 95.49 Mc/sec. Higher-order diagrams involving three or more orders of correlation interaction were investigated and found to be of minor importance in affecting the hfs constant of soidum.

I. INTRODUCTION

The Brueckner-Goldstone (BG) many-body linked-cluster perturbation theory[1,2] has been applied successfully[3-9] in the past to the study of hyperfine properties of a number of atomic systems. This method is especially suitable for the hyperfine-structure (hfs) problem for three main reasons. First, it allows various types of correlation effects, which are usually neglected in conventional one-electron theory, to be treated systematically by a perturbation procedure utilizing a suitably chosen orthonormal basis set. Secondly, the use of diagrammatic techniques in this method enables one to gain considerable physical insight and assess the relative importance of the contributions to hfs from different physical processes, such as exchange core-polarization (ECP), inter- and intra-shell correlations, self-consistency, and mutual polarization of orbitals. Thirdly, being a perturbation theory, it handles small quantities rather than the differences of large up- and down-spin densities as in the unrestricted Hartree-Fock (UHF) theory.[10] The most remarkable example where these techniques have been demonstrated to be particularly successful is the phosphorus atom,[7] where the BG many-body procedure has not only provided good agreement in magnitude with experiment but has also removed the discrepancy in sign that was found with the UHF theory.[11]

The purpose of the present paper is to report the results of our calculation on the hfs constant A (in the spin-Hamiltonian term $A\vec{I}\cdot\vec{J}$) for atomic sodium in its ground state (^2S). Accurate experimental data are available for A in this atom,[12] but no calculations for A incorporating many-body effects are available in the literature. However, one-electron calculations are available for the direct and core-polarization effects in this atom, the latter through UHF as well as perturbation procedures[13,14] based on a differential equation approach. It is interesting to inquire into how these results compare with those from the one-electron BG diagrams and the nature of many-body effects as well as the comparison with experiment of the total result by the BG procedure.

In Sec. II, we present very briefly the pertinent features of BG theory as applied here to hfs calculations. Section III involves a description of all the important diagrams and our results for the sodium atom. Section IV contains the discussion and comparison of our results with earlier one-electron results and experiments.

II. THEORY

A. Resume of BG Theory

The total nonrelativistic Hamiltonian for an atomic system of N electrons is

$$\mathcal{H}=\sum_{i=1}^{N} T_i+\sum_{i<j} v_{ij} \quad , \tag{1}$$

where T_i represents the sum of the kinetic energy