

Hyperfine structure constants of low-lying levels of ^{173}Yb .

Even parity levels									
	3D_1 (5d6s)	3D_2 (5d6s)	3D_3 (5d6s)	1D_2 (5d6s)	3S_1 (6s7s)	3D_1 (6s6d)	3D_2 (6s6d)	3D_3 (6s6d)	1D_2 (6s6d)
	A (MHz)								
Val.(2e)	443	-288	-348	62	-1489	633	-468	-437	238
Total	596	-351	-420	131	-1938	838	-683	-569	392
Exper.	563	-362	-430	100	-1873	818.7	-732.5	-559.9	438.5
	B (MHz) ^a								
Val.(2e)	156	229	368	676	0.3	38	55	92	115
Total	290	440	728	1086	0.2	58	96	150	184
Exper.	335	482	909	1115	< 3	59.3	52.5	139.6	142.2
Odd parity levels									
	$^3P_1^o$ (6s6p)	$^3P_2^o$ (6s6p)	$^1P_1^o$ (6s6p)	$^3P_1^o$ (6s7p)	$^3P_2^o$ (6s7p)				
	A (MHz)								
Val.(2e)	-765	-556	98	-1044	-666				
Total	-1094	-745	191	-1488	-871				
Exper.	-1094.1	-738	59	-1144	-854				
	B (MHz) ^a								
Val.(2e)	-533	860	428	-80	163				
Total	-822	1335	848	-111	264				
Exper.	-826.5	1312	605	12	267				

^a Electric quadrupole moment is taken to be 2.80 b.

Hyperfine structure constants of low-lying levels of ^{137}Ba .

	3D_1	3D_2	3D_3	1D_2	$^3P_1^o$	$^3P_2^o$	$^1P_1^o$
A (MHz)							
Val.(2e)	-353	306	350	- 25	794	595	- 46
Total	-547	405	443	-102	1160	845	-107
Exper.	-521	416	457	- 82	1151	—	-109
B (MHz) ^a							
Val.(2e)	12.5	18.1	31.9	39.7	-26.6	47.0	26.8
Total	17.7	26.8	47.4	67.2	-43.2	77.4	58.4
Exper.	17.9	25.9	47.4	59.6	-41.6	—	51

^a Electric quadrupole moment is taken to be 0.245 b.

Hyperfine structure constant A of low-lying levels of ^{205}Tl .

	$6p_{1/2}$	$6p_{3/2}$	$7s_{1/2}$	$7p_{1/2}$	$7p_{3/2}$	$6d_{3/2}$	$6d_{5/2}$
Val.(3e)	18466	-14	11310	1863	308	-127	315
Total	21623	264	12307	2157	315	-35	184
Exper.	21311	265	12297	2155	309	-43	229

Hyperfine structure constants A and A_d , P,T-odd parameters W_d and W_S and anapole moment parameter W_A for diatomic molecules.

Molecule	Method	Ref.	A (MHz)	A_d (MHz)	W_d ($10^{25} \frac{\text{Hz}}{\text{e}\cdot\text{cm}}$)	W_S (kHz)	W_A (Hz)
^{137}BaF	Exper. Semiempir.	[1]	2326	25	-0.41	-13	240
		[2]	2418	17	-0.35	-11	210
	Theory: valence		1466	11	-0.22	-6	107
	Theory: total		2224	24	-0.36	-10	175
^{171}YbF	Exper. Semiempir.	[3]	7617	102	-1.26	-43	650
	Theory: valence		4854	60	-0.91	-33	486
	Theory: total		7839	94	-1.21	-43	634
	DF+PT	[4]	7865	60	-0.60	-21	310
	unrestricted DF	[5]			-1.20	-22	
^{199}HgF	Exper. Semiempir.	[6]	22127	247	-4.7	-203	2700

1. Knight L B, Easley W C and Weltner W 1971 *J. Chem. Phys.* **54**, 322
2. Ryzlewicz C *et al.* 1982 *Chem. Phys.* **71** 389
3. Knight L B, Jr. and Weltner W, Jr. 1970 *J. Chem. Phys.* **53** 4111
4. Quiney H M, Skaane H and Grant I P 1998 *J. Phys. B* **31** L85
5. Parpia F A 1998 *J. Phys. B* **31** 1409
6. Knight L B, Fisher T A and Wise M B 1981 *J. Chem. Phys.* **74**, 6009

Effective operators for valence electrons.

All-electron Schrödinger equation is equivalent to the following equation for the valence electrons with the effective Hamiltonian:

$$\begin{aligned} H_{\text{eff}}\Phi &= E\Phi, \\ H_{\text{eff}} &= P(H + V'R_Q(E)V')P, \end{aligned}$$

where P is projector on a valence subspace and $Q = 1 - P$, V' is the operator of the residual Coulomb interaction and $R_Q(E)$ is the Green's function in Q -subspace:

$$\begin{aligned} V' &= H - H_0, \\ R_Q(E) &= Q \frac{1}{E - QHQ} Q. \end{aligned}$$

In the lowest order of the perturbation theory the operator H_{eff} is calculated with zero order Green's function

$$R_Q^0(E) = Q \frac{1}{E - QH_0Q} Q.$$

Solution of the wave equation with H_{eff} can be used to find different observables, if corresponding effective operators for valence electrons are formed:

$$A_{\text{eff}} \approx PAP + PV'R_Q^0(E)A_{\text{rpa}}P + PA_{\text{rpa}}R_Q^0(E)V'P,$$

where A_{rpa} corresponds to the random-phase approximation. This expression does not include so-called structural radiation and large number of high order corrections.

Semiempirical wave function for YbF molecule.

We assume that wave function of the ground state of YbF has the form:

$$|\Sigma, \omega\rangle = |\sigma_s, \omega\rangle + \delta_f \overline{|\sigma_f, -\omega\rangle},$$

where $\omega = \pm\frac{1}{2}$ is the projection of the total electronic angular momentum on the molecular axis and the bar over the orbital corresponds to the hole. More explicitly many electron wave function reads

$$|\Sigma, \omega\rangle = [\dots] \left(|\sigma_f, -\frac{1}{2}\rangle |\sigma_f, \frac{1}{2}\rangle |\sigma_s, \omega\rangle + \delta_f |\sigma_f, \omega\rangle |\sigma_s, -\frac{1}{2}\rangle |\sigma_s, \frac{1}{2}\rangle \right).$$

When spin-orbit interaction is taken into account, this wave function becomes:

$$|\Sigma, \omega\rangle = |\sigma_s, \omega\rangle + c_p |\pi_p, \omega\rangle + \delta_f \overline{|\sigma_f, -\omega\rangle} + c_f \overline{|\pi_f, -\omega\rangle}.$$

We can expand molecular orbitals in spherical waves with the origin at the Yb nucleus:

$$\begin{aligned} |\sigma_s, \omega\rangle &= (x_s |\tilde{6}s\rangle + x_p |\tilde{6}p_0\rangle + x_d |\tilde{5}d_0\rangle + \dots) |\omega\rangle, \\ |\sigma_f, \omega\rangle &= (|\tilde{4}f_0\rangle + \varepsilon_d |\tilde{5}d_0 + \dots\rangle) |\omega\rangle, \\ |\pi_p, \omega\rangle &= (a_p |\tilde{6}p_{2\omega}\rangle + \dots) |-\omega\rangle, \\ |\pi_f, \omega\rangle &= (|\tilde{4}f_{2\omega}\rangle + \dots) |-\omega\rangle. \end{aligned}$$

Let us try to reduce the number of free parameters in the wave function for the ground state. First, we can estimate mixing coefficients c_p and c_f :

$$c_p = \frac{\langle \pi_p, \omega | H_{so} | \sigma_s, \omega \rangle}{E_X - E_A} \approx \frac{x_p a_p \xi_{6,1}}{\sqrt{2}(E_X - E_A)},$$

$$c_f = \delta_f \frac{\langle \pi_f, -\omega | H_{so} | \sigma_f, -\omega \rangle}{E_X - E_F} \approx \frac{-\sqrt{3}\delta_f \bar{\xi}_{4,3}}{E_X - E_F},$$

where $\xi_{n,l}$ denotes spin-orbit constant for the shell n, l of Yb^+ ion:

$$\xi_{6,1} = 1900 \text{ cm}^{-1}, \quad \bar{\xi}_{4,3} = -3665 \text{ cm}^{-1}.$$

We can use experimental data on the spin-doubling constant to exclude one more parameter of the wave function.

$$\gamma = 2B \left(1 - \langle \Sigma(X), \frac{1}{2} | J_{e,+} | \Sigma(X), -\frac{1}{2} \rangle \right),$$

where $\mathbf{J}_e = \mathbf{L} + \mathbf{S}$ is the total angular momentum of the electrons. For the pure Σ state $\langle \mathbf{J}_e \rangle = \langle \mathbf{S} \rangle$ and we have $\gamma = 0$. This is no longer true, when the spin-orbit corrections are taken into account. It is easy to calculate γ :

$$\gamma = 2B \left(2(x_p a_p)^2 \frac{\xi_{6,1}}{E_X - E_A} + 12\delta_f^2 \frac{\bar{\xi}_{4,3}}{E_X - E_F} \right).$$

This equation gives the following relation between x_p and δ_f :

$$2100x_p^2 - 11150\delta_f^2 = 13, \quad \Rightarrow \quad \delta_f^2 \approx 0.19x_p^2.$$

Now we can use experimental data on hyperfine structure constants A and A_d to fix the remaining parameters of the wave function.

$$\begin{aligned} A &= (11850x_s^2 - 102x_p^2 - 5x_d^2) \text{ MHz} = 7617 \text{ MHz}, \\ A_d &= (486x_p^2 + 36x_d^2) \text{ MHz} = 102 \text{ MHz}, \end{aligned}$$

Solution of these equations is:

$$x_s = 0.80; \quad x_p = 0.45, \quad x_d \leq 0.4.$$

Now we can use these numbers to calculate parameter W_d :

$$\begin{aligned} W_d &= (-29.7x_sx_p + 1.3x_px_d + \dots) \text{ au} \\ &= -10.2 \text{ au} = -1.26 \cdot 10^{25} \text{ Hz}/(\text{e cm}). \end{aligned}$$