Radical Pair Recombination Reactions

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Introduction

This note walks through the quantum mechanics in your paper on the semiclassical theory of radical pair recombination reactions.

Calculation

Consider the simplest case of single nuclear spin of $I = 1/2$ with no external field

$$H = a\,\mathbf{S}\cdot\mathbf{I} \tag{1}$$

Note the following

$$\mathbf{S}\cdot\mathbf{I}|S\rangle = -\frac{3}{4}|S\rangle \tag{2}$$

$$\mathbf{S}\cdot\mathbf{I}|T_\alpha\rangle = \frac{1}{4}|T_\alpha\rangle \tag{3}$$

$$S_z|S\rangle = \frac{1}{2}|T_0\rangle \tag{4}$$

$$S_z|T_0\rangle = \frac{1}{2}|S\rangle \tag{5}$$

where $|S\rangle$ and $|T_{+,0,-}\rangle$ are singlet and triplet states, respectively.
hence

$$\boxed{R_{zz}(t) = \frac{1}{4}(1+\cos at)} \tag{6}$$

In the presence of external field

$$H = \omega S_z + a\,\mathbf{S}\cdot\mathbf{I} \tag{7}$$

The eigenstates are

$$|1\rangle = |T_+\rangle \tag{8}$$

$$|2\rangle \equiv |\Gamma_+\rangle = \cos\theta|T_0\rangle + \sin\theta|S\rangle \tag{9}$$

$$|3\rangle \equiv |\Gamma_-\rangle = -\sin\theta|T_0\rangle + \cos\theta|S\rangle \tag{10}$$

$$|4\rangle = |T_-\rangle \tag{11}$$

The eigenvalues are

$$E_1 = \frac{\omega}{2} + \frac{a}{4} \tag{12}$$

$$E_2 = \frac{\Omega}{2} - \frac{a}{4} \tag{13}$$

$$E_3 = -\frac{\Omega}{2} - \frac{a}{4} \tag{14}$$

$$E_4 = -\frac{\omega}{2} + \frac{a}{4} \tag{15}$$

where $\Omega \equiv \sqrt{\omega^2 + a^2}$ and $\tan 2\theta \equiv \omega/a$
Note the following matrix elements

$$\langle T_\pm|S_z|T_\pm\rangle = \pm\frac{1}{2} \tag{16}$$

$$\langle \Gamma_\pm|S_z|\Gamma_\pm\rangle = \pm\frac{1}{2}\sin 2\theta = \pm\frac{\omega}{2\Omega} \tag{17}$$

$$\langle \Gamma_+|S_z|\Gamma_-\rangle = \frac{1}{2}\cos 2\theta = \frac{a}{2\Omega} \tag{18}$$

hence

$$\begin{aligned} R_{zz}(t) &= \frac{1}{2}\sum_n \langle n|S_z e^{iHt} S_z e^{-iHt}|n\rangle \\ &= \frac{1}{2}\sum_{nm} |\langle n|S_z|m\rangle|^2 e^{i(E_m - E_n)t} \end{aligned} \tag{19}$$

$$\boxed{R_{zz}(t) = \frac{1}{4}\Big[1 + \left(\frac{\omega}{\Omega}\right)^2 + \left(\frac{a}{\Omega}\right)^2 \cos\Omega t\Big]} \tag{20}$$

By allowing $\theta \to 0$, (6) is recovered.
Note the following matrix elements

$$\langle T_\pm|S_\pm|\Gamma_\pm\rangle = \langle \Gamma_\pm|S_\mp|T_\pm\rangle = \frac{1}{\sqrt{2}}(\cos\theta - \sin\theta) \tag{21}$$

$$\mp\langle T_\pm|S_\pm|\Gamma_\mp\rangle = \pm\langle \Gamma_\pm|S_\pm|T_\mp\rangle = \frac{1}{\sqrt{2}}(\cos\theta + \sin\theta) \tag{22}$$

notice that

$$R_{++}(t) = R_{--}(t) = 0 \tag{23}$$

$$2(R_{xx}(t) + iR_{xy}(t)) = R_{-+}(t) = R_{+-}(-t) = R^*_{+-}(t) \tag{24}$$

hence

$$\boxed{R_{xx}(t) = \frac{1}{4}\cos\frac{at}{2}\left[\left(1+\frac{\omega}{\Omega}\right)\cos\frac{\Omega+\omega}{2}t + \left(1-\frac{\omega}{\Omega}\right)\cos\frac{\Omega-\omega}{2}t\right]} \tag{25}$$

$$\boxed{R_{xy}(t) = \frac{1}{4}\cos\frac{at}{2}\left[\left(1+\frac{\omega}{\Omega}\right)\sin\frac{\Omega+\omega}{2}t - \left(1-\frac{\omega}{\Omega}\right)\sin\frac{\Omega-\omega}{2}t\right]} \tag{26}$$

Now consider the case of multiple nuclear spin with external field

$$H = \omega S_z + \sum_{\mu} a_\mu \mathbf{I}_\mu \cdot \mathbf{S} \tag{27}$$

It is difficult/impossible to solve the TISE analytically, but notice that

$$\boxed{H|n\rangle = \frac{\sigma_e}{4}\Big[2\omega + \sum_{\mu} a_\mu \sigma_\mu\Big]|n\rangle + \frac{1}{4}\sum_{\mu} a_\mu (1 - \sigma_e \sigma_\mu)|n + \sigma_e 2^\eta (1 - 2^{-\mu})\rangle} \tag{28}$$

where $\sigma_{e/\mu} = 2m_{S/I_\mu}$ and $|n\rangle$ is $|\sigma_e \sigma_{I_1} \cdots \sigma_{I_\eta}\rangle$ in the denary via the relabeling $\uparrow \rightarrow 0$, $\downarrow \rightarrow 1$, $n = 0, 1, \ldots, 2^{\eta+1} - 1$ and $\mu = 1, 2, \ldots, \eta$.

Hence, time propagation can be carried out without constructing the Hamiltonian (see Algorithm 1).

furthermore

$$\boxed{[H, F_z] = 0} \tag{29}$$

where $\mathbf{F} = \mathbf{S} + \sum_\mu \mathbf{I}_\mu$

Hence, the energy and the projection of total spin on z-axis can be specified simultaneously and precisely. There exists a complete set of mutual eigenstates $\{|N, M_F\rangle\}$ that satisfy

$$H|N, M_F\rangle = E_N |N, M_F\rangle \tag{30}$$

$$F_z |N, M_F\rangle = M_F |N, M_F\rangle \tag{31}$$

Algorithm 1: The Hamiltonian subroutine

```fortran
subroutine H(psi, Hpsi, a, omega)
  real(dp), intent(in)  :: psi(:), a(:), omega
  real(dp), intent(out) :: Hpsi(:)
  integer :: i, k, partner, ebit, kbit, D
  real(dp) :: se, sm, diag, amp

  D = size(psi)
  Hpsi = 0.0_dp
  ebit    = ishft(1, n_spins)

  do i = 0, D-1
    amp = psi(i+1)
    if (abs(amp) < 1.0e-12_dp) cycle
    se = merge(+1.0_dp, -1.0_dp, .not. btest(i, n_spins))
    diag = se * (omega*0.5_dp)
    do k = 1, n_spins
      sm    = merge(+1.0_dp, -1.0_dp, .not. btest(i, k-1))
      diag = diag + se * 0.25_dp * a(k) * sm
      if (btest(i, n_spins) .neqv. btest(i, k-1)) then
        kbit    = ishft(1, k-1)
        partner = ieor(i, ior(ebit, kbit))
        Hpsi(partner+1) = Hpsi(partner+1) + 0.5_dp * a(k) * amp
      end if
    end do
    Hpsi(i+1) = Hpsi(i+1) + diag * amp
  end do
end subroutine H
```

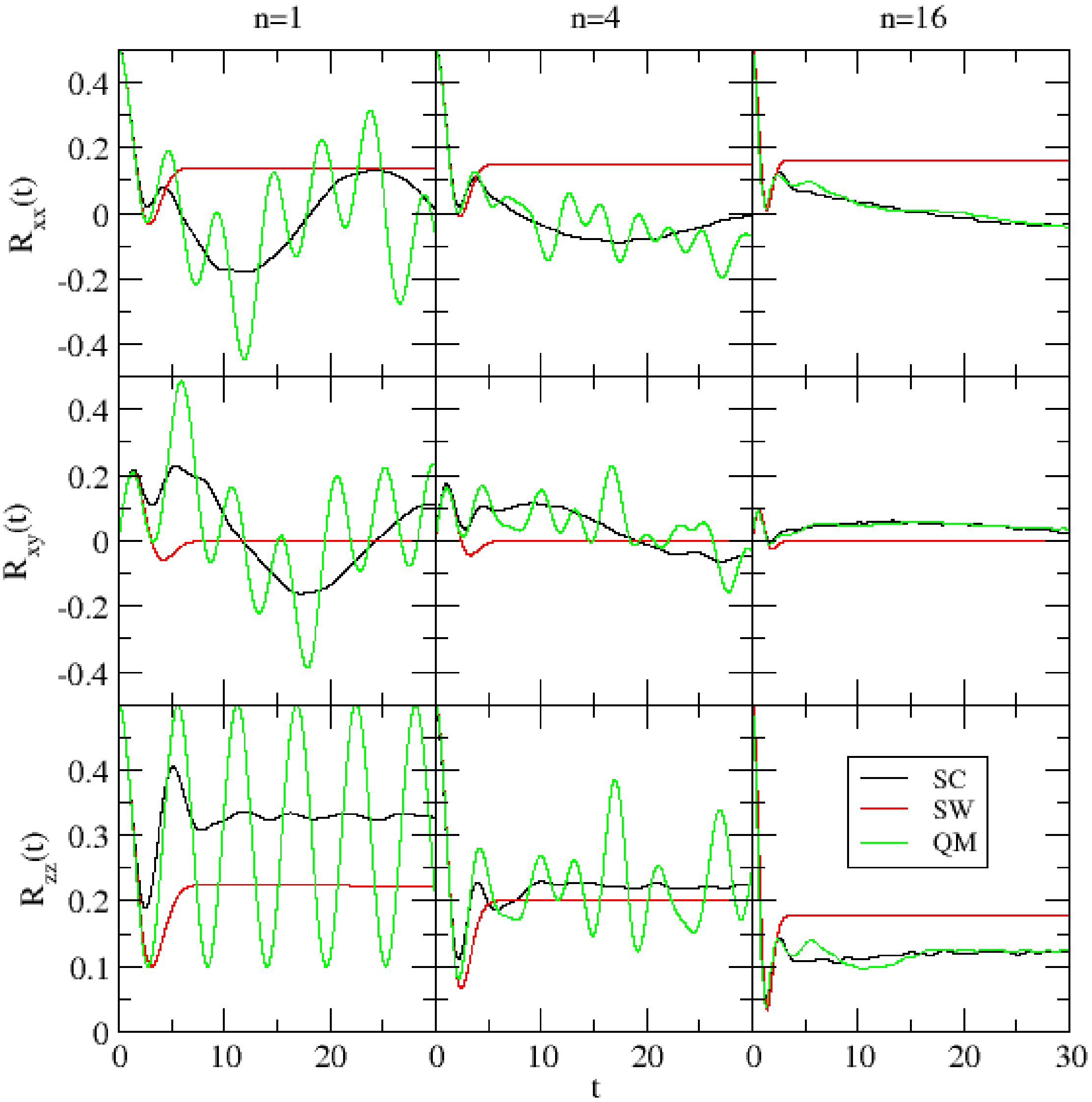

Figure 1: Electron spin correlation tensors

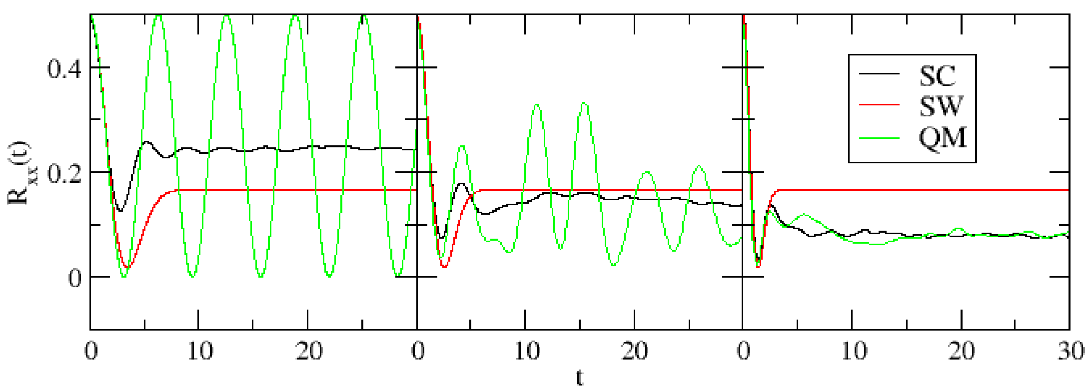

Figure 2: Electron spin correlation tensors (No external field)