

1. Problem 13.3, Schwabl [*term symbols for transition metals*]
2. [*Thomas-Fermi model*]
 - (a) Read section 13.4 on the Thomas-Fermi model of the atom.
 - (b) Show that $\chi(x) = 144/x^3$ is an exact solution to (13.67).
 - (c) Explain why this is not the solution chosen in (13.68).
 - (d) For a neutral atom in the Thomas-Fermi model, the atomic radius—defined as the location where the density drops to zero—is infinite. Using the approximation $\chi(x) = 144/x^3$, compute the radius beyond which there is exactly one electron. How does this radius depend upon Z ? This could be taken to define the size of the Thomas-Fermi atom.
3. The “dissociation energy” required to separate a D_2 molecule into two deuterium atoms (4.54 eV) is more than that for an H_2 molecule (4.46 eV).
 - (a) Explain in physical terms why the dissociation energy is about 2% more for D_2 than for H_2 , even though the proton and deuteron are practically indistinguishable to the electrons, and the bond lengths in the two molecules differ by only $\sim 0.1\%$ (0.741Å for H_2 and 0.742Å for D_2 , according to a NIST table).
 - (b) Use the above dissociation energies to estimate the zero-point energy of vibration in the H_2 and D_2 molecules, assuming that the total energy is equal to an electronic energy E_{el} that is the same for both molecules, plus a harmonic oscillator zero point energy for the nuclear vibration.
 - (c) Estimate the rms nuclear vibration amplitude in the ground state of H_2 using the result from part (b), and compare this amplitude to the bond length, and to the formula on the right hand side of Schwabl (15.6).
 - (d) Any idea why the bond length for D_2 is the longer one? (I don’t know the answer.)
4. The van der Waals interaction of two hydrogen atoms arises at second order in perturbation theory, and is thus necessarily attractive in the ground state. It decreases as $1/R^6$, since it involves the square of the leading order, $1/R^3$ term in the $1/R$ expansion of the interatomic potential, Schwabl (15.47b). But let’s look more closely at *first* order in perturbation theory, to determine whether there could be a lower or equal order term that could contribute. It turns out the story is rather surprising: the attractive nature of the interaction of two neutral atoms is accidental, in the following sense.¹

¹I learned about this from the paper <https://arxiv.org/abs/1401.8141>

Consider the first order perturbation $\langle 00|W|00\rangle$ (Schwabl's notation) in any spatial dimension $d \geq 2$, keeping the same form for the potential.²

- (a) Show that, for any d , parity symmetry of the unperturbed atomic ground states implies vanishing of the $1/R^3$ contribution, as well as all the even order, $1/R^{2n}$, contributions to $\langle 00|W|00\rangle$.
- (b) Show that the $1/R^5$ term has expectation value $(3e^2/4R^5)(d-3)(d-5)\langle x_1^2 x_2^2 \rangle$, where x_1 is one of the Cartesian coordinates for atom 1 and similarly for x_2 . This vanishes in $d = 3$, justifying the tacit assumption that the lowest order effect arises at second order in perturbation theory,³ but it is nonvanishing in dimensions other than 3 and 5, and is *repulsive* in $d = 2$ or $d > 5$ dimensions!

[*Hints* for (b): i. Using spherical symmetry of the atomic states, express all the non-vanishing terms as multiples of $\langle 0|x_1^2 x_2^2|0\rangle$. ii. The series expansion can be done by hand without too much difficulty, if you are careful. Alternatively, or to check yourself, you can use, Mathematica (or some other software). All UMD students have access to a free Mathematica license, which can be obtained from `terpware.umd.edu`.]

²We consider this form even though it would not follow from the natural generalization of Maxwell's equations in other dimensions. We exclude $d = 1$ since the $1/r$ potential is too singular in one dimension.

³As you might suspect, there is a good reason for the vanishing in $d = 3$, and in fact this happens to all orders in $1/R$. It can be traced to the fact that the potential outside a spherical charge distribution vanishes if the total charge vanishes. The explanation isn't quite so simple, however, since the charge distribution extends arbitrarily far from the atom. The atom has a size $\sim a$, and our real expansion parameter is the dimensionless ratio a/R . Choosing units with $a = 1$, we just expand in $1/R$. The perturbation expansion is blind to the possibility that \vec{x}_1 could fail to be outside the electron distribution of atom 2, since in effect we are expanding about $R = \infty$.