

**HOMEWORK ASSIGNMENT 5**  
**QUANTUM MECHANICS**  
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**1. Prove the following vector calculus identities.**

Let  $(\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3)$  be the standard basis of  $\mathbb{R}^3$  and  $\cdot$  the standard dot product. Let  $\partial_i$  be the scalar operator  $\partial/\partial x_i$ . Let  $\varepsilon_{ijk}$  be the Levi-Civita symbol, so  $\mathbf{a} \times \mathbf{b} = \sum_{ijk} \varepsilon_{ijk} \mathbf{e}_i a_j b_k$ , where  $a_i := \mathbf{e}_i \cdot \mathbf{a}$  and  $b_i := \mathbf{e}_i \cdot \mathbf{b}$ . We use without further comment the fact that two vectors are equal if their projections onto  $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$  coincide. The indices  $i, j, k$  always run from 1 to 3.

(a)  $\nabla(fg) = f\nabla g + g\nabla f$ . We have

$$\begin{aligned} \mathbf{e}_i \cdot (\nabla(fg)) &= \partial_i(fg) = f\partial_i(g) + g\partial_i(f) \\ &= \mathbf{e}_i \cdot (f\nabla g) + \mathbf{e}_i \cdot (g\nabla f) = \mathbf{e}_i \cdot (f\nabla g + g\nabla f). \end{aligned}$$

(b)  $\nabla \cdot (\mathbf{a} \times \mathbf{b}) = -\mathbf{a} \cdot (\nabla \times \mathbf{b}) + \mathbf{b} \cdot (\nabla \times \mathbf{a})$ . We have

$$\begin{aligned} \nabla \cdot (\mathbf{a} \times \mathbf{b}) &= \sum_{ijk} \varepsilon_{ijk} \partial_i (a_j b_k) = \sum_{ijk} (\varepsilon_{ijk} a_j \partial_i b_k + \varepsilon_{ijk} b_k \partial_i a_j) = \sum_{ijk} \varepsilon_{ijk} a_j \partial_i b_k - \sum_{ijk} \varepsilon_{ijk} b_j \partial_i a_k \\ &= \mathbf{a} \cdot \left( \sum_{ijk} \varepsilon_{ijk} \mathbf{e}_j \partial_i b_k \right) - \mathbf{b} \cdot \left( \sum_{ijk} \varepsilon_{ijk} \mathbf{e}_j \partial_i a_k \right) = -\mathbf{a} \cdot (\nabla \times \mathbf{b}) + \mathbf{b} \cdot (\nabla \times \mathbf{a}). \end{aligned}$$

(c)  $\nabla \times (\mathbf{a} \times \mathbf{b}) = (\mathbf{b} \cdot \nabla) \mathbf{a} - (\mathbf{a} \cdot \nabla) \mathbf{b} + (\nabla \cdot \mathbf{b}) \mathbf{a} - (\nabla \cdot \mathbf{a}) \mathbf{b}$ .

$$\begin{aligned} \mathbf{e}_i \cdot (\nabla \times (\mathbf{a} \times \mathbf{b})) &= \sum_{jk} \varepsilon_{ijk} \partial_j (\mathbf{e}_k \cdot (\mathbf{a} \times \mathbf{b})) = \sum_{jk} \varepsilon_{ijk} \partial_j \left( \sum_{lm} \varepsilon_{klm} a_l b_m \right) \\ &= \sum_{jk} \varepsilon_{ijk} \left( \sum_{lm} \varepsilon_{klm} a_l \partial_j b_m \right) + \sum_{jk} \varepsilon_{ijk} \left( \sum_{lm} \varepsilon_{klm} b_m \partial_j a_l \right) \\ &= \sum_j (a_i \partial_j b_j - a_j \partial_j b_i) + \sum_j (b_j \partial_j a_i - b_i \partial_j a_j) \\ &= \sum_j (b_j \partial_j a_i + a_i \partial_j b_j) - \sum_j (a_j \partial_j b_i + b_i \partial_j a_j) \\ &= \sum_j (b_j \partial_j + \partial_j b_j) a_i - \sum_j (a_j \partial_j + \partial_j a_j) b_i \\ &= \mathbf{e}_i \cdot ((\mathbf{b} \cdot \nabla) \mathbf{a} + (\nabla \cdot \mathbf{b}) \mathbf{a} - (\mathbf{a} \cdot \nabla) \mathbf{b} - (\nabla \cdot \mathbf{a}) \mathbf{b}). \end{aligned}$$

(From the second to the third lines we use several times the equality  $\sum_{jk} \varepsilon_{ijk} x_{i,j,k} = \sum_{s=\pm 1} s x_{i,i+s,i-s}$ , where arithmetic on indices is cyclic, that is, 4 means 1 and 0 means 3.)

(d)  $\nabla \cdot (\nabla \times \mathbf{b}) = 0$ . With the same convention on indices,

$$\nabla \cdot (\nabla \times \mathbf{b}) = \sum_{ijk} \varepsilon_{ijk} \partial_i (\partial_j b_k) = \sum_k (\partial_{k+1} \partial_{k-1} b_k - \partial_{k-1} \partial_{k+1} b_k) = 0.$$

(e)  $\nabla \times (\nabla f) = 0$ . Again because  $\partial_j$  and  $\partial_k$  commute,

$$\mathbf{e}_i \cdot (\nabla \times (\nabla f)) = \sum_{jk} \varepsilon_{ijk} \partial_j (\mathbf{e}_k \cdot (\nabla f)) = \sum_{jk} \varepsilon_{ijk} \partial_j \partial_k f = 0.$$

**2a.** For a constant (i.e., uniform) magnetic field  $\mathbf{B}$ , explicitly verify that it can be represented by the vector potential  $\mathbf{A} = \frac{1}{2} \mathbf{B} \times \mathbf{r}$  as  $\mathbf{B} = \nabla \times \mathbf{A}$ .

Using 1c:

$$\nabla \times (\frac{1}{2} \mathbf{B} \times \mathbf{r}) = \frac{1}{2} ((\mathbf{r} \cdot \nabla) \mathbf{B} + (\nabla \cdot \mathbf{r}) \mathbf{B} - (\mathbf{B} \cdot \nabla) \mathbf{r} - (\nabla \cdot \mathbf{B}) \mathbf{r}).$$

Since  $\mathbf{B}$  does not depend on  $\mathbf{r}$ , the first and last term on the right-hand side vanish; moreover  $\nabla \cdot \mathbf{r} = 3$  and  $\mathbf{B} \cdot \nabla = (\sum_i B_i \partial_i) (\sum_j r_j \mathbf{e}_j) = \sum_{ij} B_i \partial_i r_j \mathbf{e}_j = \sum_{ij} B_i \delta_{ij} \mathbf{e}_j = \mathbf{B}$ . Hence the right-hand side reduces to  $\frac{1}{2} (3\mathbf{B} - \mathbf{B}) = \mathbf{B}$ .

**2b.** What is form of the vector potential for a magnetic field directed along the  $z$  axis?

$$\frac{1}{2} (-By, Bx, 0).$$

**2c.** Show that the addition of the gradient of a scalar potential  $f$  to this vector potential reproduces the same magnetic field.

This is true for  $\mathbf{B} = \nabla \times \mathbf{A}$ , whether or not  $\mathbf{B}$  is constant: adding to  $\mathbf{A}$  the gradient of a function does not change  $\nabla \times \mathbf{A}$  because any gradient is irrotational (see 1f).

**2d.** The electric field is derived from a scalar potential  $\phi$  and the vector potential  $\mathbf{A}$  according to  $\mathbf{E} = -\nabla\phi - \partial\mathbf{A}/\partial t$ . How must the scalar potential be modified to reproduce the same electric field when the vector potential is modified as in (b)? [presumably this should be (c)?]

Suppose we add to  $\mathbf{A}$  a gradient  $\nabla\psi$ ; then we must subtract from the scalar potential  $\phi$  the function  $\partial\psi/\partial t$ , so that the changes in  $\mathbf{E} = -\nabla\phi - \partial\mathbf{A}/\partial t$  cancel out. (Note that differentiation with respect to  $t$  commutes with taking the gradient.)

**3a.** An electron is in an atomic orbital  $\chi$ , centered at the origin, and is subject to a uniform magnetic field  $\mathbf{B}$ . Let the energy of the atom at this point be  $E$ . Evaluate the energy when the atom is displaced a distance  $y$  from the origin.

**Notation:** Let the displacement vector be  $\mathbf{R}_0$  (“a distance  $y$  from the origin” is a bit ambiguous). Assume that  $\mathbf{B}$  points in the  $z$  direction (since  $\mathbf{R}_0$  is arbitrary this implies no loss of generality).

The semiclassical hamiltonian for one electron is

$$H = \frac{1}{2} (-i\nabla + \mathbf{A}(\mathbf{r}))^2 + V,$$

where  $V$  denotes the Coulomb interactions, which are not affected by a rigid displacement of the system. The kinetic term is affected because the vector potential changes from  $\mathbf{A}(\mathbf{r}) = \frac{1}{2} \mathbf{B} \times \mathbf{r}$  to

$$\mathbf{A}'(\mathbf{r}) := \mathbf{A}(\mathbf{r} + \mathbf{R}_0) = \mathbf{A}(\mathbf{r}) + \frac{1}{2} \mathbf{B} \times \mathbf{R}_0. \quad (*)$$

The change in the Hamiltonian is therefore

$$\begin{aligned} \Delta H &= \frac{1}{2} ((-i\nabla + \mathbf{A}')^2 - (-i\nabla + \mathbf{A})^2) \\ &= \frac{1}{2} ((-i\nabla)^2 - i\nabla \cdot \mathbf{A}' - 2i\mathbf{A}' \cdot \nabla + \mathbf{A}'^2 - (-i\nabla)^2 + i\nabla \cdot \mathbf{A} + 2i\mathbf{A} \cdot \nabla - \mathbf{A}^2) \\ &= \frac{1}{2} (-2i(\mathbf{A}' - \mathbf{A}) \cdot \nabla + (\mathbf{A}'^2 - \mathbf{A}^2)) \\ &= -\frac{1}{2} i(\mathbf{B} \times \mathbf{R}_0) \cdot \nabla + \frac{1}{4} (\mathbf{B} \times \mathbf{R}_0) \cdot (\mathbf{B} \times \mathbf{r}) + \frac{1}{8} |\mathbf{B} \times \mathbf{R}_0|^2. \end{aligned}$$

Assuming  $\chi$  is normalized, the change in the energy is

$$\Delta E = \langle \chi | \Delta H | \chi \rangle = \frac{1}{2} (\mathbf{B} \times \mathbf{R}_0) \cdot \langle \mathbf{p} \rangle + \frac{1}{4} (\mathbf{B} \times \mathbf{R}_0) \cdot (\mathbf{B} \times \langle \mathbf{r} \rangle) + \frac{1}{8} |\mathbf{B} \times \mathbf{R}_0|^2,$$

where  $\langle \mathbf{r} \rangle$  and  $\langle \mathbf{p} \rangle$  are the expectations of the position and (zero-field) momentum. If the orbital is “centered” at the origin in the sense that the electron density is symmetric with respect to the origin, this reduces to  $\frac{1}{8} |\mathbf{B} \times \mathbf{R}_0|^2$ .

**3b.** Repeat your evaluation of the energy of the atom after displacement when the atom is described by  $|\chi\rangle \exp\left[i\frac{e}{2\hbar}\mathbf{B}\cdot(\mathbf{y}\times\mathbf{r})\right]$ . This transformation defines a “London orbital”. Discuss briefly the advantages of this type of orbital for use in evaluating the magnetic properties of molecules.

(Again we replace  $\mathbf{y}$  by  $\mathbf{R}_0$ .) Set  $e = \hbar = 1$  and  $\phi = \exp\left(\frac{1}{2}i\mathbf{B}\cdot(\mathbf{R}_0\times\mathbf{r})\right) = \exp(i\mathbf{A}_0\cdot\mathbf{r})$ , where  $\mathbf{A}_0 = \frac{1}{2}\mathbf{B}\times\mathbf{R}_0$ . Because the  $V$  part of the Hamiltonian, being multiplicative, contributes the same to the energy whether or not the wavefunction is multiplied by the phase factor  $\phi$ , we can write the desired energy difference as

$$\Delta E = \langle\chi\phi|T'|\chi\phi\rangle - \langle\phi|T|\phi\rangle,$$

where  $T = \frac{1}{2}(-i\nabla + \mathbf{A})^2$  and likewise for  $T'$ ,

For this calculation of  $\Delta E$ , the expression for  $\Delta H = T' - T$  found in 3a turns out not to be very useful, since we’re evaluating the operators on different wavefunctions. Instead we write

$$\langle\chi\phi|T'|\chi\phi\rangle = \langle\chi\phi|\left(\frac{1}{2}(-i\nabla + \mathbf{A}')^2\right)\phi|\chi\rangle$$

and reexpress the bracket operator on the right using the identity  $\nabla\phi = \phi\nabla + i\phi\mathbf{A}_0$ , which follows from the product rule. We have

$$(-i\nabla + \mathbf{A}')^2\phi = (-i\nabla + \mathbf{A}')\phi(-i\nabla + \mathbf{A}_0 + \mathbf{A}') = \phi(-i\nabla + \mathbf{A}_0 + \mathbf{A}')^2.$$

We’d like to say that  $\mathbf{A}_0 + \mathbf{A}' = \mathbf{A}$ , but the sign is wrong. It’ll be right if we define the London factor as the conjugate of what was given:  $\phi = \exp\left(-\frac{1}{2}i\mathbf{B}\cdot(\mathbf{R}_0\times\mathbf{r})\right)$ . Then  $T'\phi = (-i\nabla + \mathbf{A}')^2\phi = \phi(-i\nabla - \mathbf{A}_0 + \mathbf{A}')^2 = \phi(-i\nabla + \mathbf{A})^2$  and we get cancellation:

$$\Delta E = \langle\chi\phi|T'|\chi\phi\rangle = \langle\chi\phi|\phi T|\chi\rangle - \langle\phi|T|\phi\rangle = 0.$$

The advantage of London orbitals is explained in the introduction of Helgaker and Jørgensen, *J. Chem. Phys.* **95** (1991), 2595: “When a uniform external magnetic field is applied to a molecular system, the magnetic vector potential depends on the choice of gauge origin. Properties calculated using this potential are independent of the origin as long as the calculation is carried out in a complete basis. In a truncated basis, origin independence is no longer guaranteed. To impose gauge invariance in such calculations one [multiplies the atomic orbitals by the London phase factor. This makes] the individual atomic integrals independent of the gauge so that properties calculated from these integrals become origin independent.”

**4a.** Evaluate the matrix element  $\langle\sigma|\hat{H}^{(1)}|\sigma^*\rangle$  for an electric field parallel to the molecular axis in terms of atomic orbital contributions, to allow you to determine whether the result is zero or non-zero.

The perturbation hamiltonian is  $H^{(1)} = -\mathcal{E}\cdot\boldsymbol{\mu}$ , where  $\boldsymbol{\mu}$  is the dipole moment operator, equal to  $\sum_i q_i\mathbf{r}_i = -\sum_i \mathbf{r}_i$ . Write  $\sigma = \phi_A + \phi_B$  and  $\sigma^* = \phi_A - \phi_B$ .

Let the molecule be oriented along the  $z$ -axis, with charges at  $z = d$  and  $z = -d$ . Then  $H^{(1)} = \mathcal{E}(z_1 + z_2)$ . By symmetry,  $\langle\phi_A|z|\phi_A\rangle = d$ ,  $\langle\phi_B|z|\phi_B\rangle = -d$ ,  $\langle\phi_A|z|\phi_B\rangle = 0$ . Therefore

$$\langle\sigma|z|\sigma^*\rangle = \frac{1}{2}\langle\phi_A + \phi_B|z|\phi_A - \phi_B\rangle = \frac{1}{2}(d + d) = d,$$

and the result is indeed nonzero; there will be mixing of  $\sigma^*$  with the ground state even in first order.

**4b.** Repeat for an electric field perpendicular to the molecular axis. Say the field is directed along the  $x$ -axis. In this case we must consider instead the products  $\langle\phi_A|x|\phi_A\rangle = 0$ ,  $\langle\phi_B|x|\phi_B\rangle = 0$ ,  $\langle\phi_A|x|\phi_B\rangle = 0$ . There is no change (to first order) in the ground state wavefunction when the electric field is applied.

**4c.** Use first order perturbation theory to discuss the form of the occupied orbital in the presence of applied fields parallel and perpendicular to the molecular axis. The first order correction to the ground-state wavefunction is

$$\Phi^{(1)} = \sum'_n \frac{\langle\Phi_n^{(0)}|H^{(1)}|\Phi_0^{(0)}\rangle}{E_0^{(0)} - E_n^{(0)}} |\Phi_n^{(0)}\rangle,$$

which in our case, using the equalities  $\langle \sigma^* | z | \sigma \rangle = d$  and  $\langle \sigma^* | x | \sigma \rangle = 0$  from 4a and 4b, reduces to

$$\Psi_{//}^{(1)} = \frac{\mathcal{E}d}{E_{\sigma^*} - E_{\sigma}} \sigma^*, \quad \Psi_{\perp}^{(1)} = 0.$$

The macroscopic dielectric strength of many solids is about  $10^7$  V/m, or  $2 \times 10^{-5}$  in atomic units. For a field of this intensity we get for the mixing-in coefficient of  $\sigma^*$  the value  $3.5 \times 10^{-5}$  (using the approximations  $d = 0.7 a_0$  and  $E_{\sigma^*} - E_{\sigma} = 0.4$  hartree).

**4d.** Discuss qualitatively how your answer would change if a second s-type basis function was added to each atom. And what about adding a shell of p-type functions to each atom?

Adding more base functions can only increase the polarizability, better adapting the wavefunction to the field. However, adding more s-type basis functions won't change the result  $\Psi_{\perp}^{(1)} = 0$ , because any linear combination of such functions still has  $\sigma$  symmetry around the molecular axis. Put another way, an electric field in the  $x$  direction cannot couple two orbitals that have cylindrical symmetry around the  $z$ -axis, and so will have no first-order effect in a basis of such orbitals. This is also true for  $p_z$  orbitals; like the  $s$  orbitals, they can only contribute to  $\Psi_{//}^{(1)}$ . But the  $p_x$  and  $p_y$  orbitals will contribute to both  $\Psi_{//}^{(1)}$  and  $\Psi_{\perp}^{(1)}$ .

**5a.** Write the perturbation theory expression for the polarizability of a 1-electron system whose eigenstates are known.

We assume the ground state.

From the definition of the polarizability  $\alpha$  as (minus) the second-derivative matrix of the energy with respect to the electric field, we can identify the product  $\mathcal{E} \cdot \alpha \cdot \mathcal{E}$  with  $-2$  times the second-order energy term  $E^{(2)}$  in the solution of the perturbation problem  $H = H^{(0)} + \lambda \mathcal{E} \cdot \mathbf{r}$ . We know (from the MP2 discussion, for example) that

$$E^{(2)} = \sum_n' \frac{\langle \phi_0^{(0)} | \mathcal{E} \cdot \mathbf{r} | \phi_n^{(0)} \rangle \langle \phi_n^{(0)} | \mathcal{E} \cdot \mathbf{r} | \phi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}.$$

Hence, for any  $i, j = 1, 2, 3$  (with  $r_i = x$  and so on) we have

$$\alpha_{ij} = -2 \sum_n' \frac{\langle \phi_0^{(0)} | r_i | \phi_n^{(0)} \rangle \langle \phi_n^{(0)} | r_j | \phi_0^{(0)} \rangle}{E_0^{(0)} - E_n^{(0)}}. \quad (\ddagger)$$

**5b.** Suppose an electron in a neutral 1-electron atom is modeled as a particle in a 1-d box of side length 1 Angstrom. Evaluate the electronic polarizability along the  $x$  axis.

Again we assume the ground state. We solve the problem for a box of length  $a$  symmetric with respect to the origin. The energy values equal  $n^2/2a^2$  and the wavefunctions are  $A \cos(n\pi x/a)$  for  $n$  odd,  $A \sin(n\pi x/a)$  for  $n$  even, where  $A = \sqrt{2/a}$ . The product  $\langle \phi_n^{(0)} | x | \phi_0^{(0)} \rangle$  equals, in absolute value,

$$\left| \frac{2}{a} \int_{-a/2}^{a/2} \cos\left(\frac{\pi x}{a}\right) \sin\left(\frac{n\pi x}{a}\right) x dx \right| = \frac{8na}{\pi^2(n^2 - 1)^2} \quad \text{for even } n,$$

and it vanishes for odd  $n > 1$ . So the contribution to the sum in  $(\ddagger)$  from the  $n$ -th wavefunction is

$$-2 \left( \frac{8na}{\pi^2(n^2 - 1)^2} \right)^2 \times \frac{2a^2}{n^2 - 1} = \frac{256a^4 n^2}{\pi^4(4n^2 - 1)^5}.$$

Summing over all  $n$  even we get  $\alpha = -0.427533a^4$ . Since  $1 \text{ \AA} = 1.890 a_0$ , the final result is  $-5.4521$  atomic units, or  $-9.0 \times 10^{-41} \text{ C}^2\text{m}^2/\text{J}$ .

**5c.** Suggest how the polarizability depends on the box length.

From the previous part:  $\alpha$  is proportional to  $a^4$ .