

**Photoionization dynamics
of
atoms and molecules**

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Part A Atomic photoionization

A-1. Atomic structure

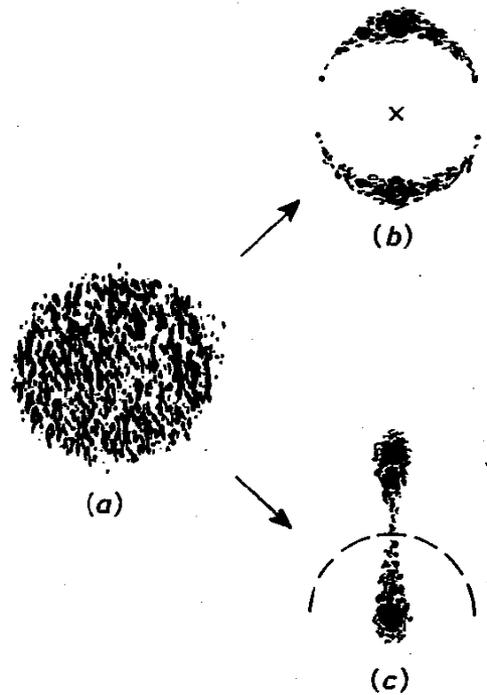
The Hamiltonian H for an atom with Z electrons is given by

$$H = -\frac{1}{2} \sum_i \nabla_i^2 - Z \sum_i \frac{1}{r_i} + \sum_{i \neq j} \frac{1}{r_{ij}} .$$

Approximating the Coulomb interactions between the electrons by a mean spherical potential $V(r)$, it follows that

$$H^0 = -\frac{1}{2} \sum_i \nabla_i^2 - Z \sum_i \frac{1}{r_i} + \sum_i V(r_i) \quad \text{and} \quad H^0 \Psi^0 = E^0 \Psi^0 .$$

The motion of electrons described by the wavefunction Ψ^0 is independent. This situation is called the *independent particle* or *single-particle* picture. The examples of the single-particle wavefunctions are those from Hartree-Fock (HF) approach. HF wavefunctions follow from a *self-consistent* procedure. Then, they represent the best wavefunctions within the independent particle model. The description of the Z -electron system by independent particle functions then leads to the shell model. However, if the Coulomb interaction between the electrons is taken more accurately into account (not by a mean-field approach), this simplified picture changes and the electrons are subject to a correlated motion which is not described by the shell model.



Angular correlation

Radial correlation

Illustration of the charge density distribution for (a) uncorrelated and (b) and (c) correlated motion of the two 1s-electrons in helium.

A-2. Photoionization dynamics

The treatment of the many-body problem which requires the inclusion of electron correlations plays a role in the formulation of not only the structure of the atom, but also that of the dynamical changes caused by any kind of interaction between the atom and other particles including radiation quanta. **The photon interaction has the special advantage of being known exactly.** For simplicity, it will be given here in the dipole approximation and in the length form;

$$O_p(\text{photoionization}) = \sum_i \boldsymbol{\varepsilon} \cdot \mathbf{r}_i,$$

where \mathbf{r}_i is the position vector of the electron i and $\boldsymbol{\varepsilon}$ is the polarization vector of the photon. The form explains the name *dipole* approximation, because the expectation value $\langle g | O_p | g \rangle$ in the ground state of $|g\rangle$ gives the atomic electric dipole moment. Because the summation index runs independently over all atomic electrons, the photon operator is a single-particle operator. As a consequence, *one* photon can interact only with *one* atomic electron.

Why can many-electron processes, ionization accompanied simultaneous excitation, direct double ionization, double excitation and so on, occur with the photon-atom interaction?

A-3. Photo-double ionization of helium atom

A calculation of the differential cross section for double ionization requires the evaluation of the matrix element M given by

$$M = \varepsilon \langle \mathbf{k}_a \mathbf{k}_b | \mathbf{r}_1 + \mathbf{r}_2 | 1s^2 \ S \rangle,$$

where \mathbf{k}_a and \mathbf{k}_b stand for the momentum vectors of the two ejected electrons. The electron spin is omitted in this expression because the electrons remain in the singlet state, i.e., the spatial wavefunctions are symmetric with respect to electron exchange. Therefore, one has

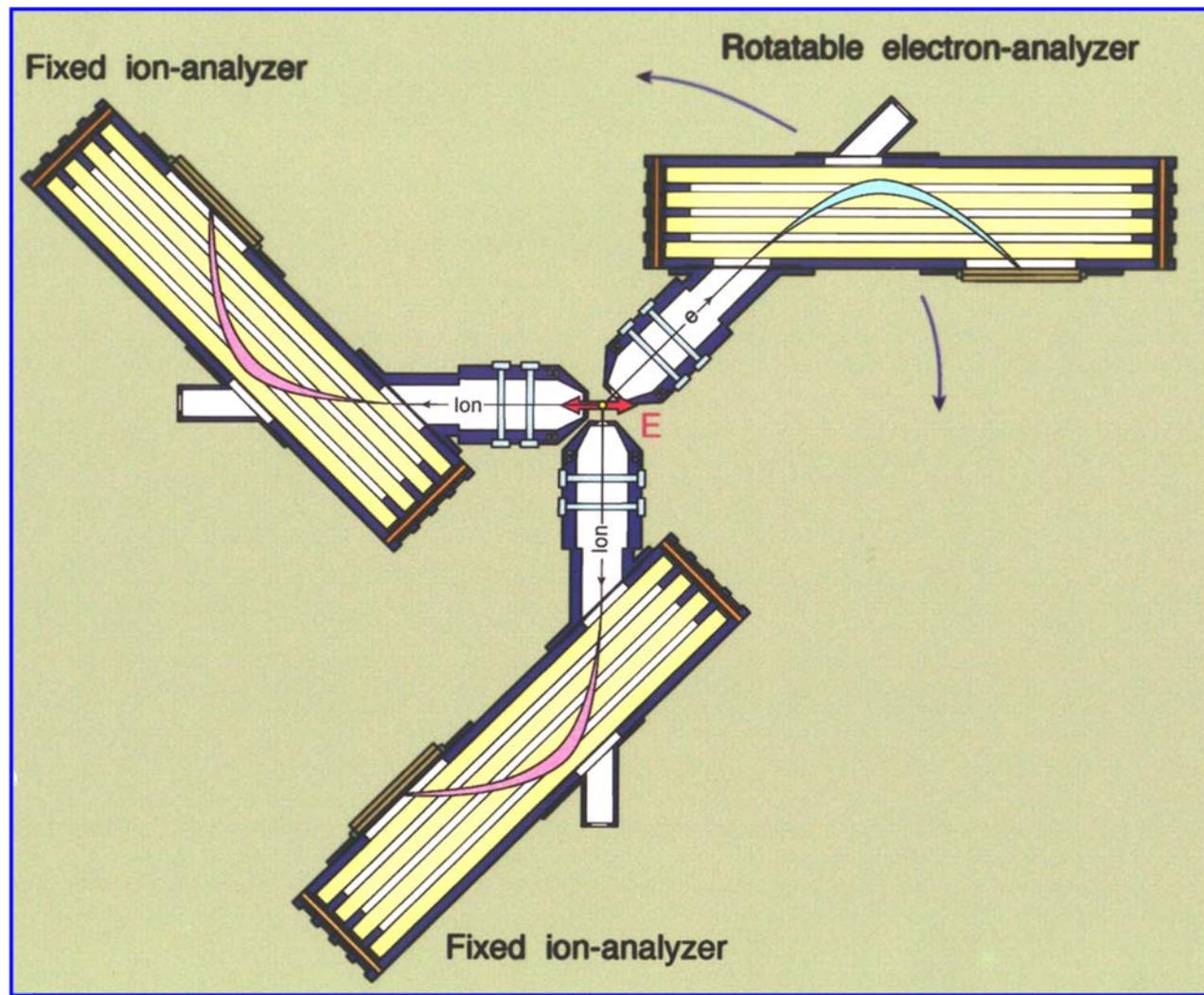
$$|1s^2 \ S \rangle = \varphi_{1s}(\mathbf{r}_1)\varphi_{1s}(\mathbf{r}_2) \quad \text{and} \quad |\mathbf{k}_a \mathbf{k}_b \rangle = \sqrt{\frac{1}{2}} \left((\varphi_{\mathbf{k}_a}(\mathbf{r}_1)\varphi_{\mathbf{k}_b}(\mathbf{r}_2) + \varphi_{\mathbf{k}_a}(\mathbf{r}_2)\varphi_{\mathbf{k}_b}(\mathbf{r}_1)) \right),$$

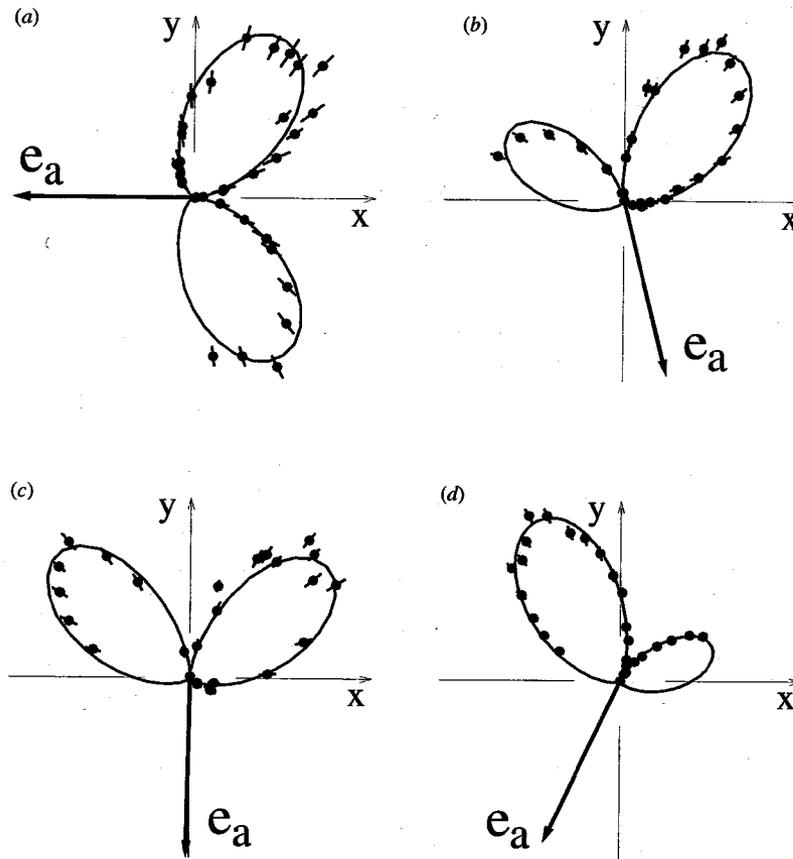
which gives

$$M = \sqrt{2}\varepsilon \langle \mathbf{k}_a | \mathbf{r}_1 | \varphi_{1s} \rangle \langle \mathbf{k}_b | \varphi_{1s} \rangle + \sqrt{2}\varepsilon \langle \mathbf{k}_b | \mathbf{r}_2 | \varphi_{1s} \rangle \langle \mathbf{k}_a | \varphi_{1s} \rangle.$$

This reflects the fact that the photon operator, as a one-particle operator, interacts with the ‘active’ 1s-electron only, ejecting it into a wave characterized by \mathbf{k}_a or \mathbf{k}_b , while the ‘passive’ 1s-electron leads to an overlap matrix element $\langle \mathbf{k} | \varphi_{1s} \rangle \neq 0$ with corresponding function of the other continuum electron. If all single-particle wavefunctions are calculated using the same Hamiltonian, these overlap matrix elements vanish due to the orthogonality of the wavefunction.

Experimental set-up for electron-electron coincidence measurements





Angular dependence of helium TDCS patterns with $E_a=E_b=10\text{eV}$.
Polarization vector of the photon is parallel to the x-axis.

The triple-differential cross section (TDCS) for photo-double ionization can be represented as

$$TDCS \propto |M|^2 = |(\cos\theta_a + \cos\theta_b)a_g + (\cos\theta_a - \cos\theta_b)a_u|^2 \quad \text{for the } ^1P \text{ final state.}$$

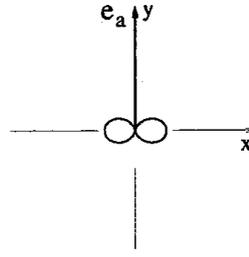
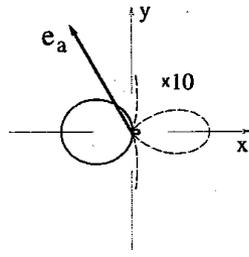
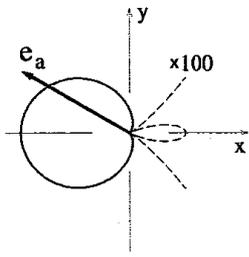
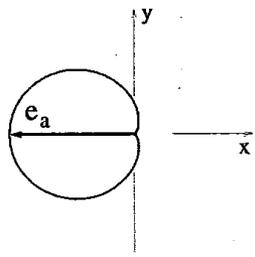
Under the exchange $k_a \leftrightarrow k_b$, one sees that

$$a_g(k_a, k_b; \theta_{ab}) = a_g(k_b, k_a; \theta_{ab}) \quad \text{and} \quad a_u(k_a, k_b; \theta_{ab}) = -a_u(k_b, k_a; \theta_{ab}),$$

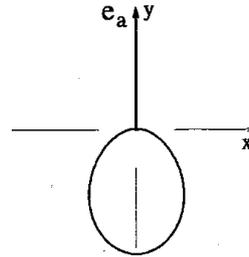
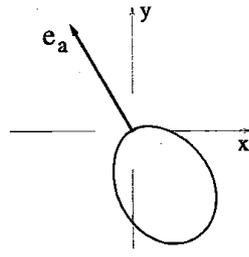
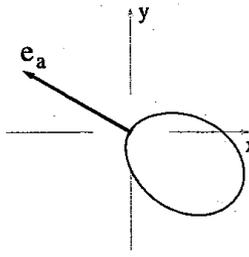
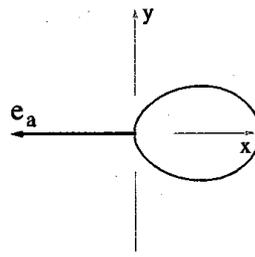
where $h\omega - IP(He^{++}) = E_a (= k_a^2/2) + E_b (= k_b^2/2)$.

The important point is that the exchange-symmetric matrix element produces a TDCS containing a portion being antisymmetric with respect to angular change $\theta_a \leftrightarrow \theta_b$, and antisymmetric with respect to energy exchange $k_a \leftrightarrow k_b$. In the special case where $k_a = k_b$, the coefficient a_u is then zero and the TDCS reduces to

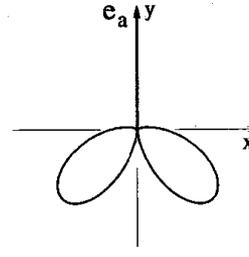
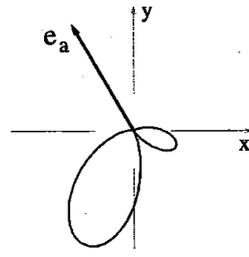
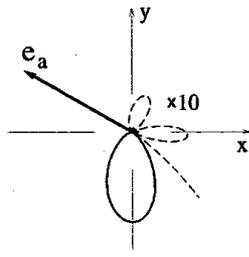
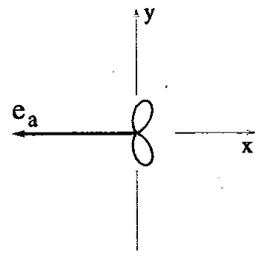
$$TDCS \propto |M|^2 = |(\cos\theta_a + \cos\theta_b)a_g|^2.$$



angular factor
($\cos\theta_a + \cos\theta_b$)



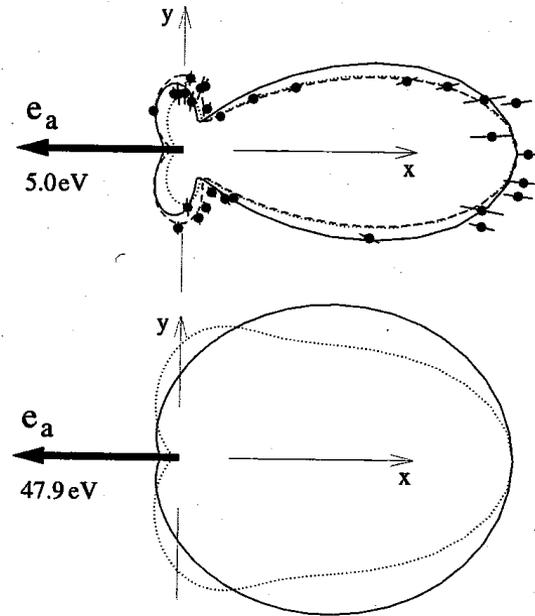
correlation factor a_g



($\cos\theta_a + \cos\theta_b$) a_g

Simulated helium TDCS patterns for the equal energy sharing of $E_a = E_b = 10\text{eV}$. Polarization vector of the photon is parallel to the x-axis. The direction of one electron, e_a , indicated by the arrow, is kept fixed for each column and takes the values $\theta_a = 180, 150, 120,$ and 90 degrees.

$$TDCS \propto |M|^2 = |(\cos\theta_a + \cos\theta_b)a_g + (\cos\theta_a - \cos\theta_b)a_u|^2$$

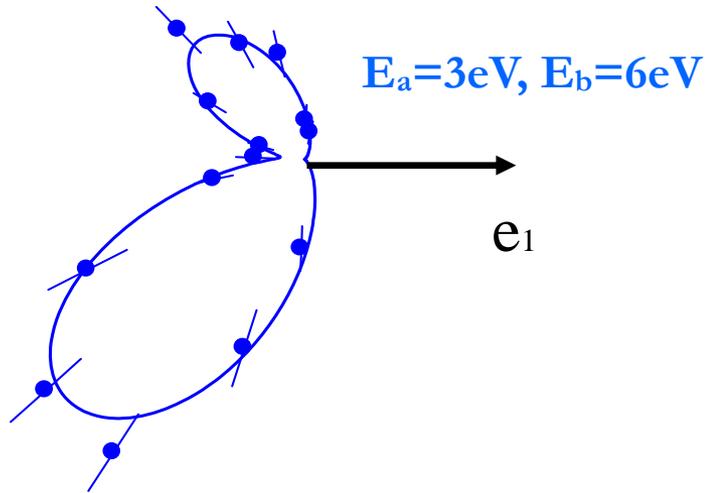


$E_a=5.0\text{eV}$ and $E_b=47.9\text{eV}$

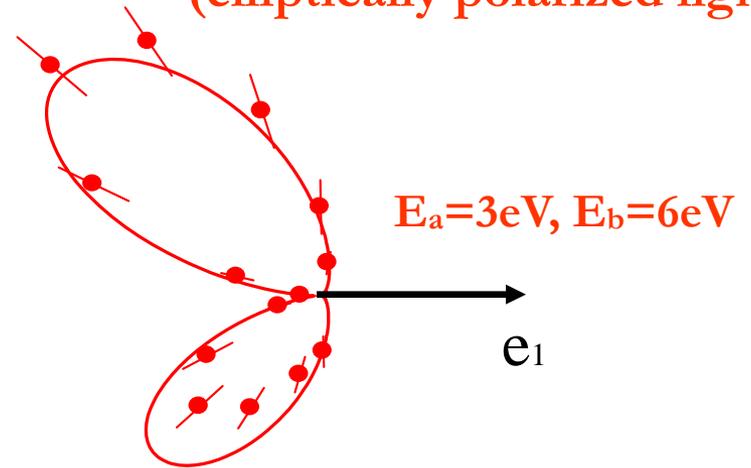
$E_a=47.9\text{eV}$ and $E_b=5.0\text{eV}$

Angular dependence of helium TDCS patterns for the unequal energy sharing condition . Polarization vector of the photon is parallel to the x-axis.

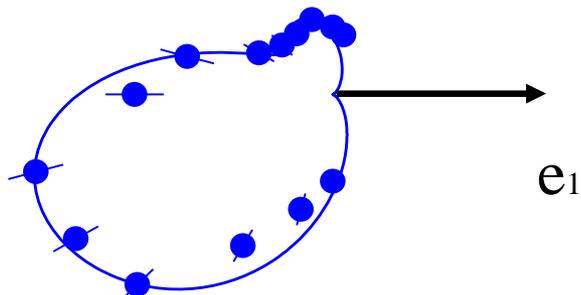
Left
(elliptically polarized light)



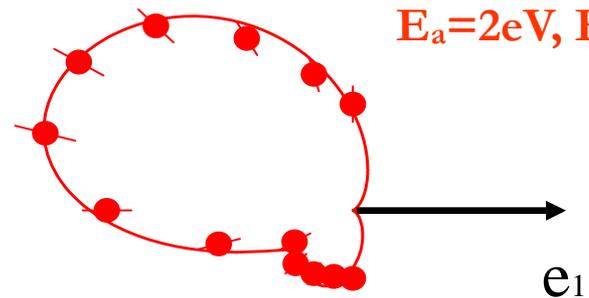
Right
(elliptically polarized light)

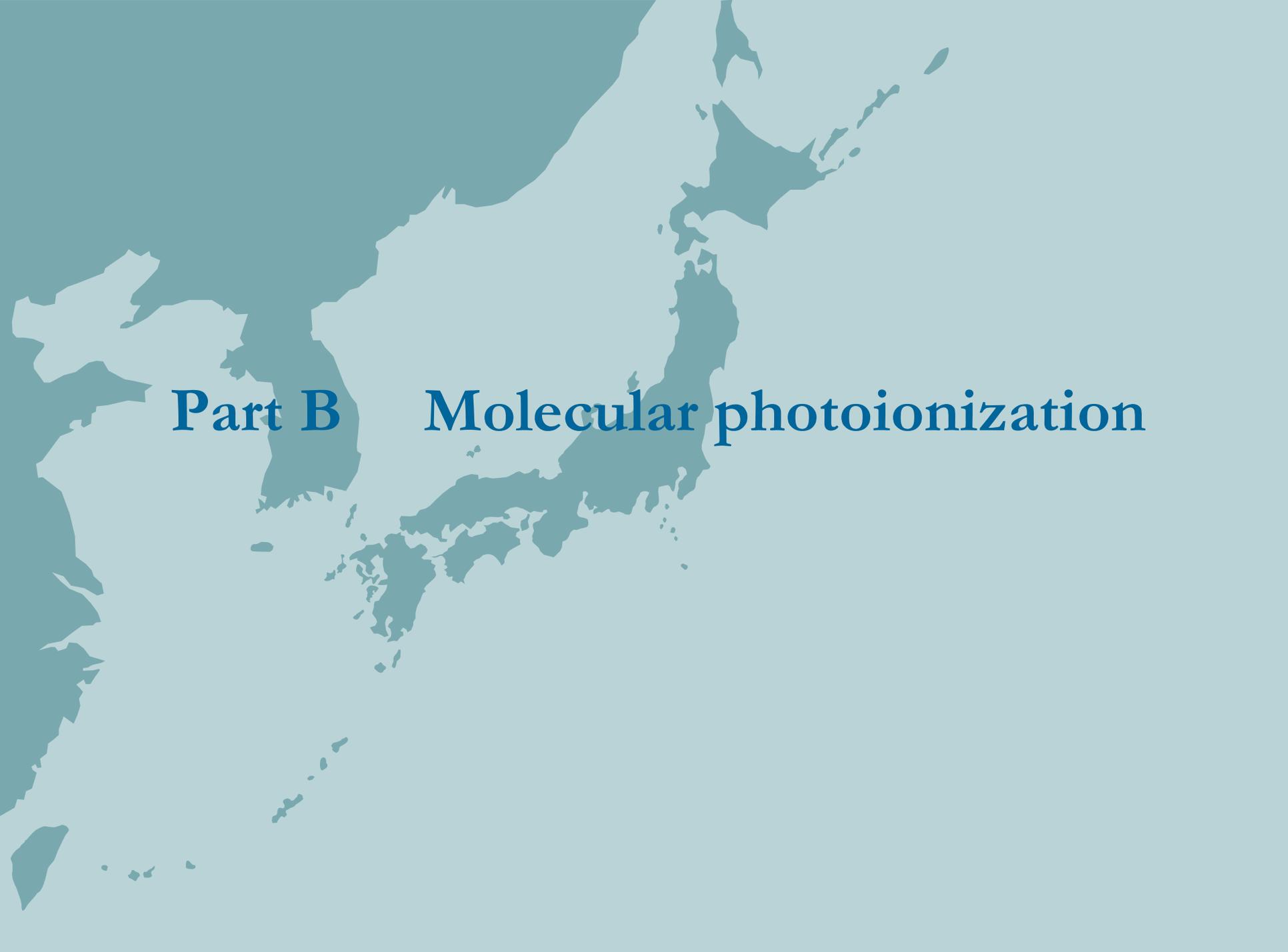


$E_a=2\text{eV}, E_b=48\text{eV}$



$E_a=2\text{eV}, E_b=48\text{eV}$

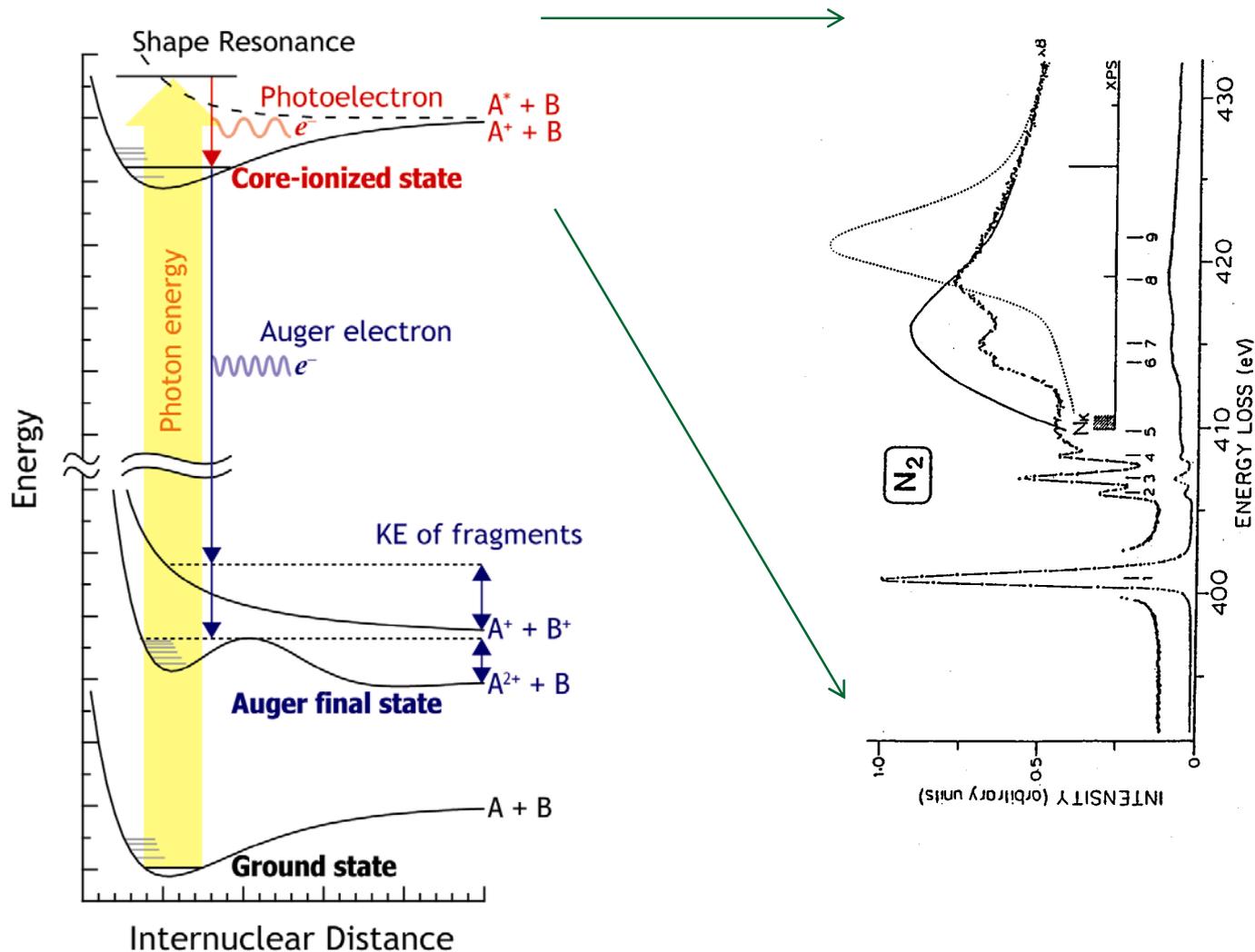




Part B

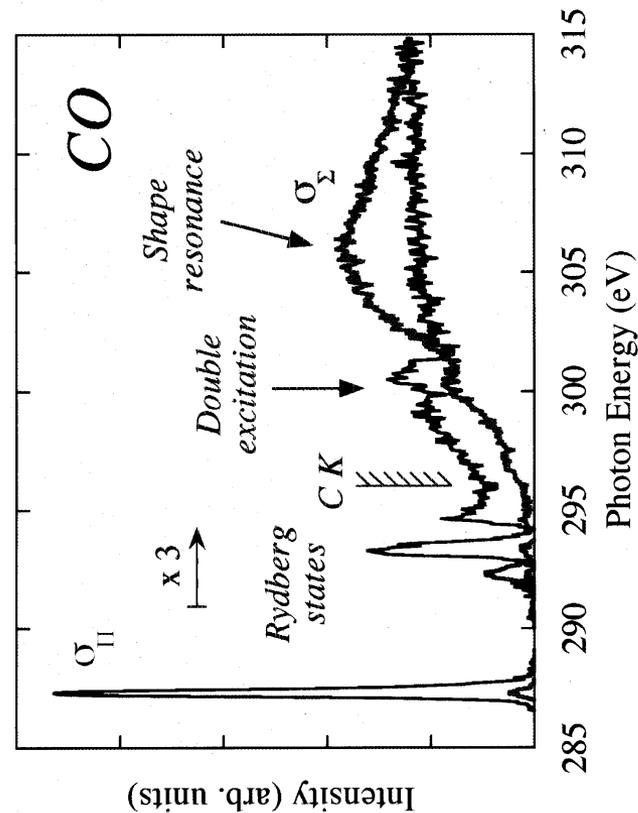
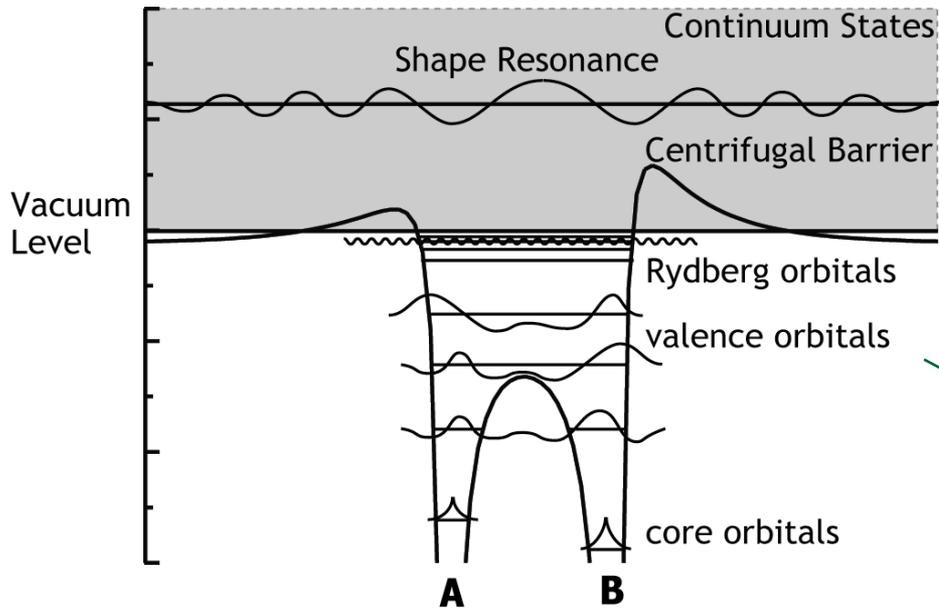
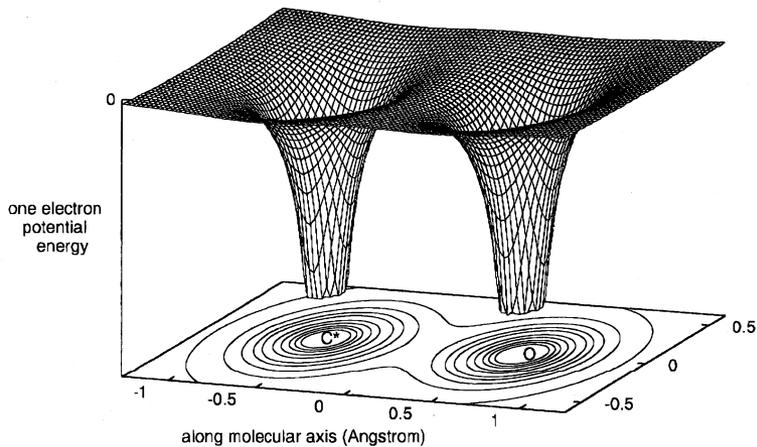
Molecular photoionization

B-1. Characteristic feature of molecular photoionization



Adiabatic molecular potential

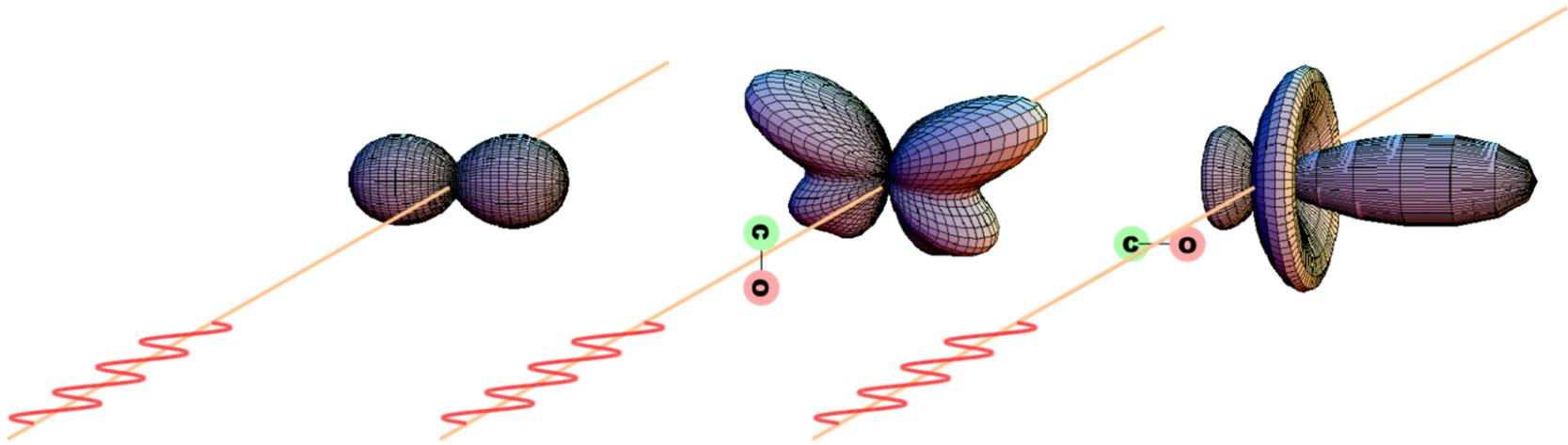
Static Exchange Potential in CO C 1s-Hole State



Effective molecular potential

B-2. Photoemission from fixed-in-space molecules

Stereographic photoelectron angular distributions for C 1s of CO



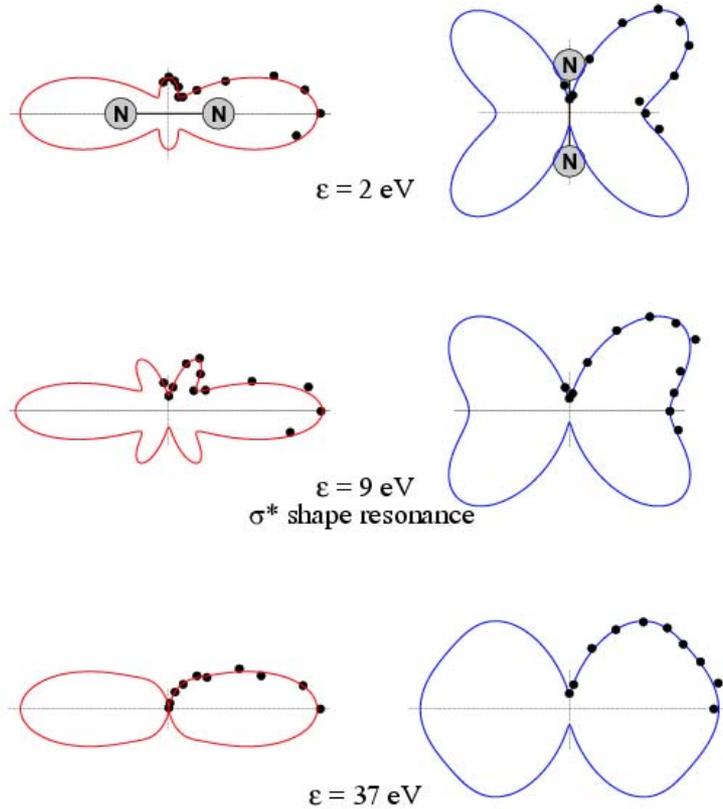
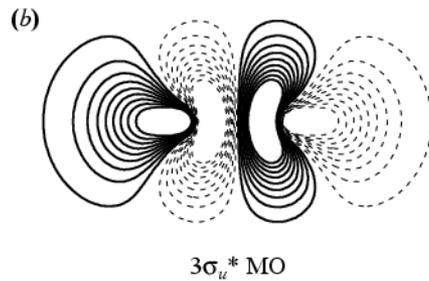
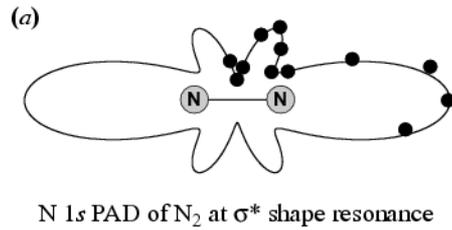
randomly oriented molecules

$$\frac{d\sigma}{d\Omega'} = \frac{\sigma}{4\pi} [1 + \beta P_2(\cos \theta')]$$

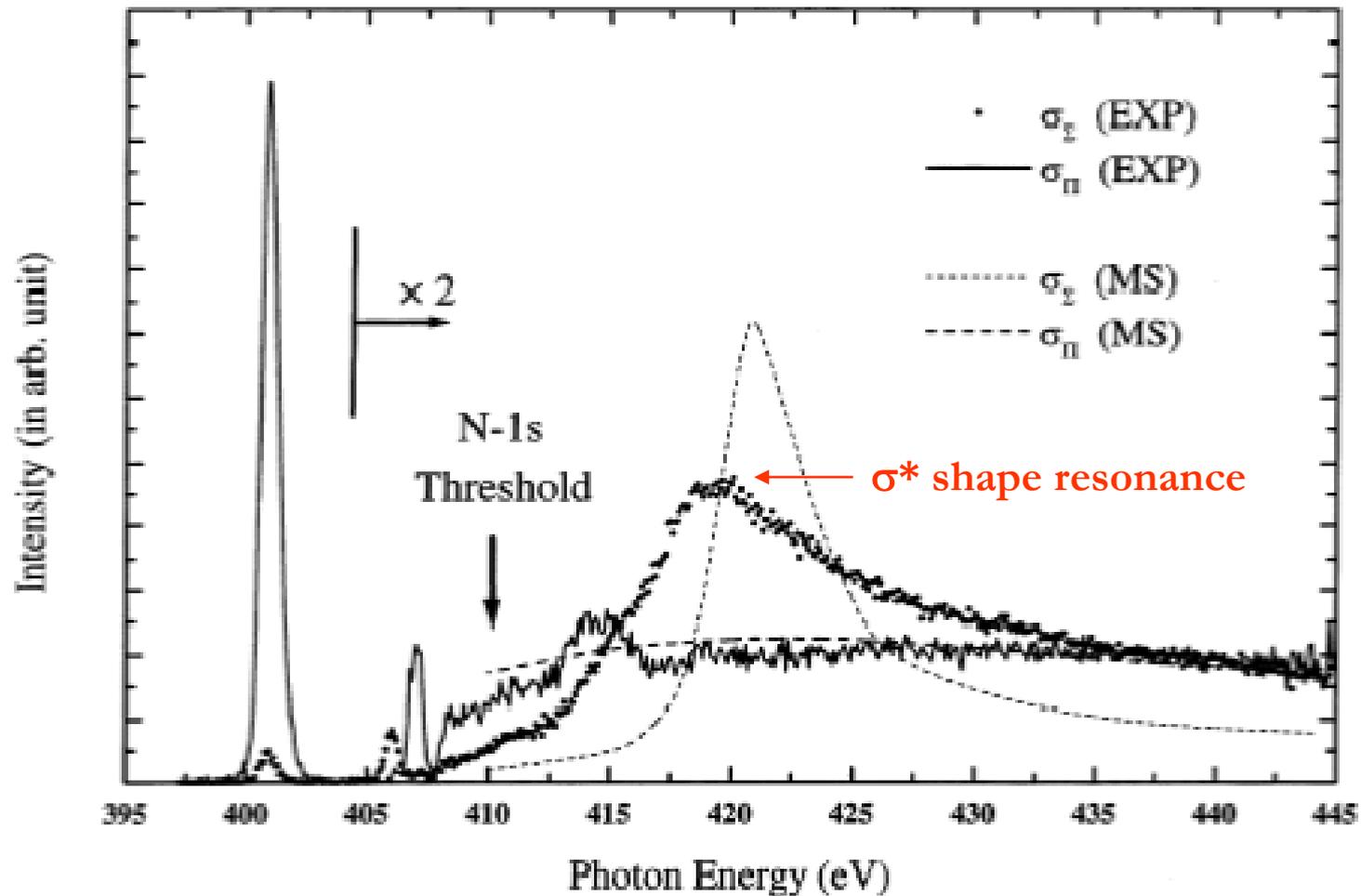
oriented molecules

$$\frac{d\sigma}{d\Omega} = \sum_{K=0}^{2\ell_{\max}} \sum_M A_{KM} Y_{KM}(\theta, \phi)$$

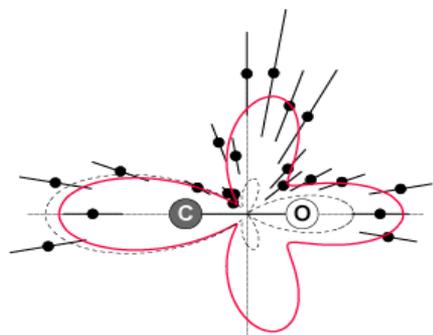
N_2 $N1s$ photoelectron angular distributions



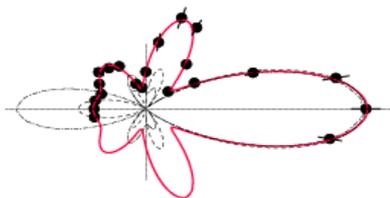
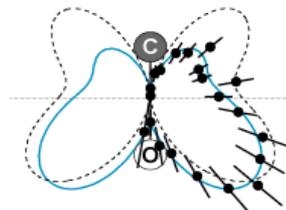
N_2 $N1s$ symmetry-resolved photoabsorption spectra



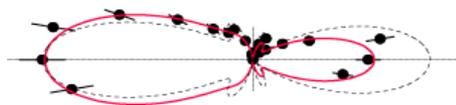
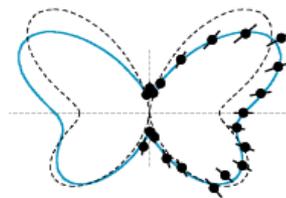
CO C1s photoelectron angular distributions



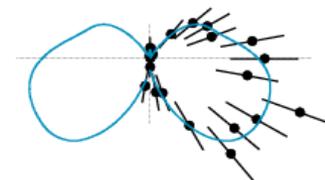
$\epsilon = 3.0 \text{ eV}$



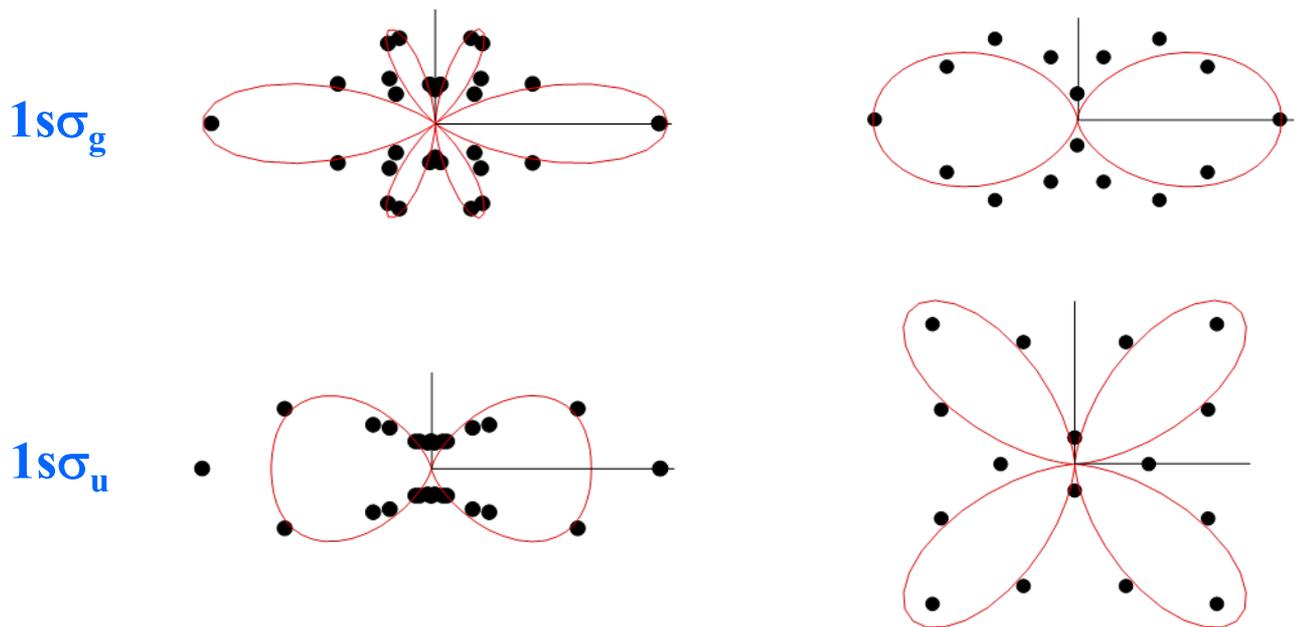
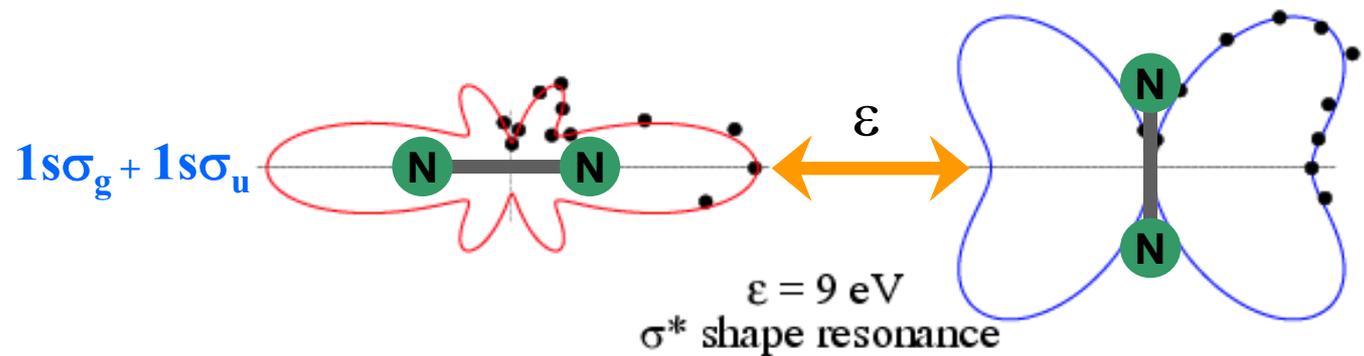
$\epsilon = 8.5 \text{ eV}$
 σ^* shape resonance



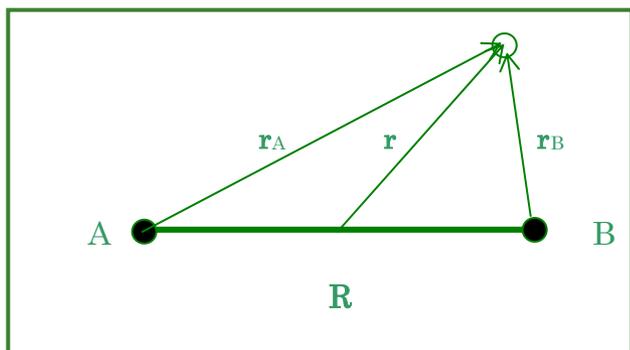
$\epsilon = 21.0 \text{ eV}$



B-3. Young's double-slit interference



Interferences in the photoionization of molecules



$$\mathbf{r}_A = \mathbf{r} + \mathbf{R}/2, \quad \mathbf{r}_B = \mathbf{r} - \mathbf{R}/2$$

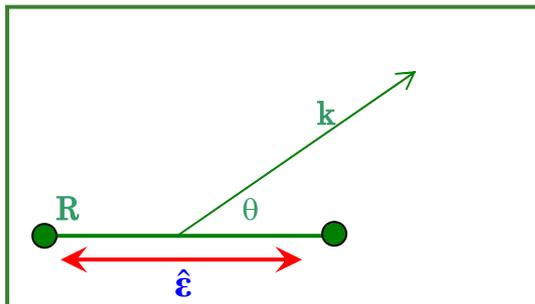
$$1s\sigma_g; \quad \phi_g(\mathbf{r}_A, \mathbf{r}_B) = \frac{1}{\sqrt{2(1+S)}} (u(\mathbf{r}_A) + u(\mathbf{r}_B)), \quad u(\mathbf{r}) = \frac{1}{\sqrt{4\pi}} 2Z^{3/2} \exp(-Zr)$$

$$1s\sigma_u; \quad \phi_u(\mathbf{r}_A, \mathbf{r}_B) = \frac{1}{\sqrt{2(1+S)}} (u(\mathbf{r}_A) - u(\mathbf{r}_B)) \quad \text{Hydrogenic } 1s \text{ wavefunction}$$

$$\begin{aligned} T_g &= \langle \exp(i\mathbf{k}\cdot\mathbf{r}) | \hat{\mathbf{e}}\cdot\mathbf{r} | \phi_g \rangle = \frac{1}{\sqrt{2(1+S)}} \left\{ \langle \exp(i\mathbf{k}\cdot\mathbf{r}) | \hat{\mathbf{e}}\cdot\mathbf{r} | u(\mathbf{r}_A) \rangle + \langle \exp(i\mathbf{k}\cdot\mathbf{r}) | \hat{\mathbf{e}}\cdot\mathbf{r} | u(\mathbf{r}_B) \rangle \right\} \\ &\propto \left\{ \langle \exp(i\mathbf{k}\cdot(\mathbf{r}_A - \mathbf{R}/2)) | \hat{\mathbf{e}}\cdot(\mathbf{r}_A - \mathbf{R}/2) | u(\mathbf{r}_A) \rangle + \langle \exp(i\mathbf{k}\cdot(\mathbf{r}_B + \mathbf{R}/2)) | \hat{\mathbf{e}}\cdot(\mathbf{r}_B + \mathbf{R}/2) | u(\mathbf{r}_B) \rangle \right\} \\ &= \left\{ \exp(i\mathbf{k}\cdot\mathbf{R}/2) + \exp(-i\mathbf{k}\cdot\mathbf{R}/2) \right\} \times \langle \exp(i\mathbf{k}\cdot\mathbf{r}) | \hat{\mathbf{e}}\cdot\mathbf{r} | u(\mathbf{r}) \rangle \\ &= 2 \cos(\mathbf{k}\cdot\mathbf{R}/2) \times \hat{\mathbf{e}} \int \exp(-i\mathbf{k}\cdot\mathbf{r}) \mathbf{r} \exp(-Zr) d\mathbf{r} \\ &= 2 \cos(\mathbf{k}\cdot\mathbf{R}/2) \times \hat{\mathbf{e}}\cdot\mathbf{k} \end{aligned}$$

$$T_u = \langle \exp(i\mathbf{k}\cdot\mathbf{r}) | \hat{\mathbf{e}}\cdot\mathbf{r} | \phi_u \rangle \propto 2 \sin(\mathbf{k}\cdot\mathbf{R}/2) \times \hat{\mathbf{e}}\cdot\mathbf{k}$$

For the $\hat{\mathbf{e}} // \mathbf{R}$ case



$$\hat{\mathbf{e}} \cdot \mathbf{k} = k \cos \theta \quad \text{and} \quad \mathbf{k} \cdot \mathbf{R} = kR \cos \theta$$

$$1s\sigma_g \rightarrow kp : \frac{d\sigma}{d\theta} = |T_g|^2 \propto k^2 \cos^2 \theta \times \cos^2 \left(\frac{1}{2} kR \cos \theta \right)$$

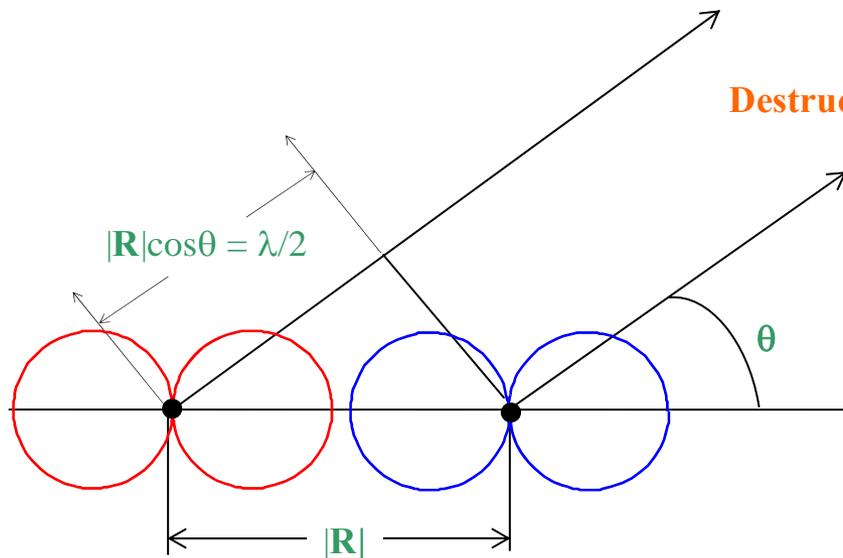
$$1s\sigma_u \rightarrow kp : \frac{d\sigma}{d\theta} = |T_u|^2 \propto k^2 \cos^2 \theta \times \sin^2 \left(\frac{1}{2} kR \cos \theta \right)$$

$1s\sigma_g \rightarrow kp$

$$\frac{1}{2} \mathbf{k} \cdot \mathbf{R} = \frac{1}{2} kR \cos \theta = \frac{\pi}{2}$$

$$R \cos \theta = \frac{\pi}{k} = \frac{\lambda}{2}$$

Destructive interference

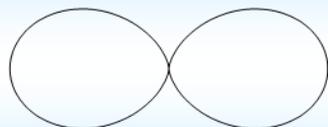


$$(\hat{\mathbf{e}} \cdot \mathbf{k})^2 = k^2 \cos^2 \theta$$

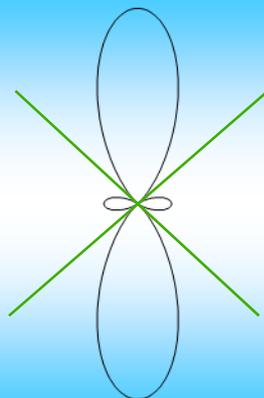
$$k^2 \cos^2 \theta$$

$$\cos^2\left(\frac{1}{2}kR \cos \theta\right)$$

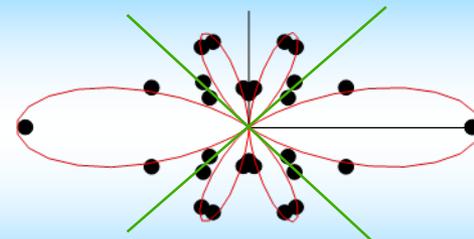
$1s\sigma_g$



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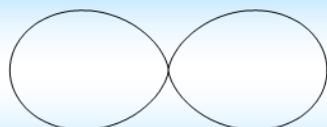
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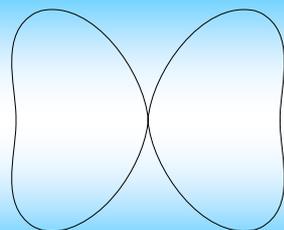
$$k^2 \cos^2 \theta$$

$$\sin^2\left(\frac{1}{2}kR \cos \theta\right)$$

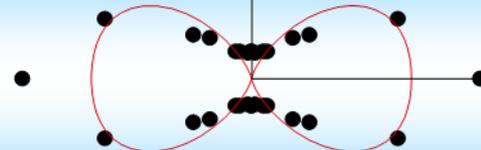
$1s\sigma_u$



×

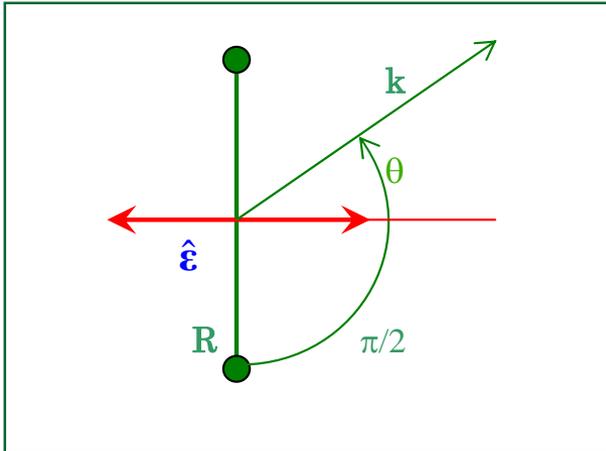


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$$R = 2.068 \text{ a.u. } k = 1.93 \text{ a.u. } (KE = 50.84 \text{ eV})$$

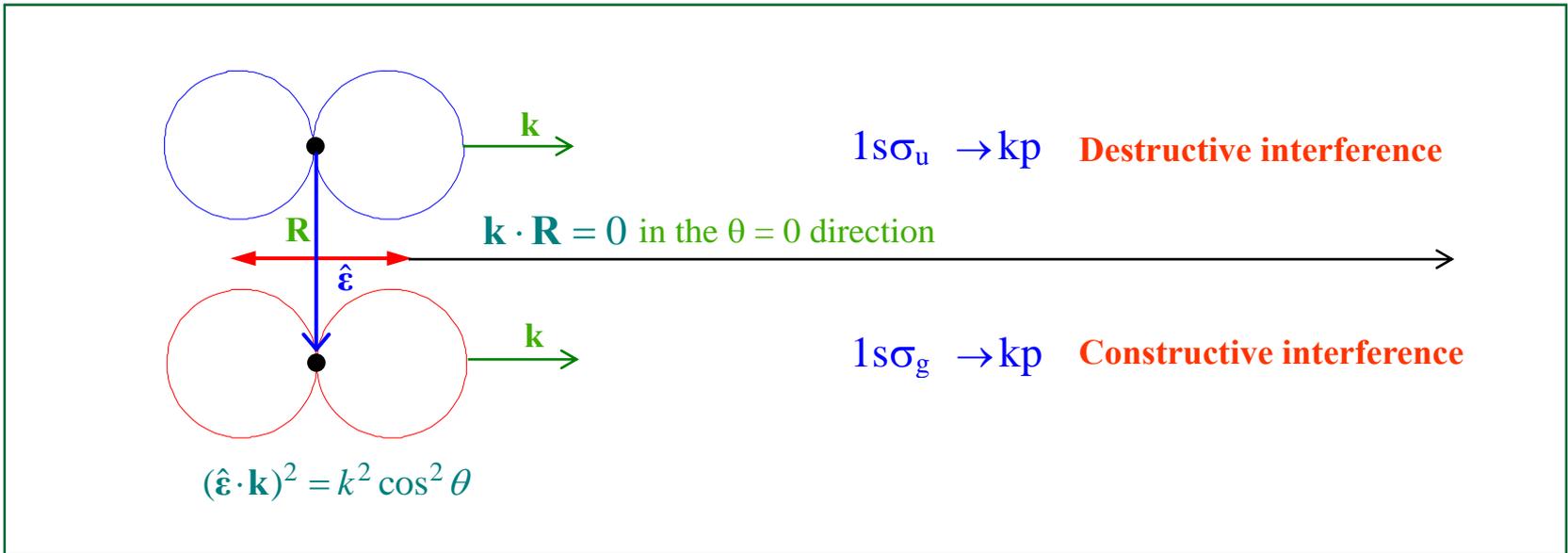
For the $\hat{\mathbf{e}} \perp \mathbf{R}$ case



$$\hat{\mathbf{e}} \cdot \mathbf{k} = k \cos \theta \quad \text{and} \quad \mathbf{k} \cdot \mathbf{R} = kR \cos(\theta + \pi/2)$$

$$1s\sigma_g \rightarrow kp : \quad \frac{d\sigma}{d\theta} \propto |T_g|^2 = k^2 \cos^2 \theta \times \cos^2 \left(\frac{1}{2} kR \cos(\theta + \frac{\pi}{2}) \right)$$

$$1s\sigma_u \rightarrow kp : \quad \frac{d\sigma}{d\theta} \propto |T_u|^2 = k^2 \cos^2 \theta \times \sin^2 \left(\frac{1}{2} kR \cos(\theta + \frac{\pi}{2}) \right)$$





Thank you for your patient.