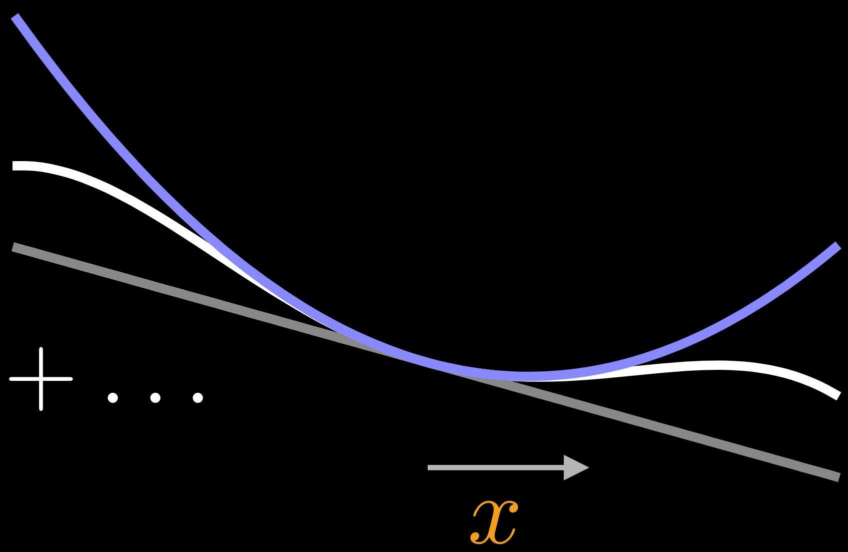
DAVID M. ROGERS, UNIV. SOUTH FLORIDA

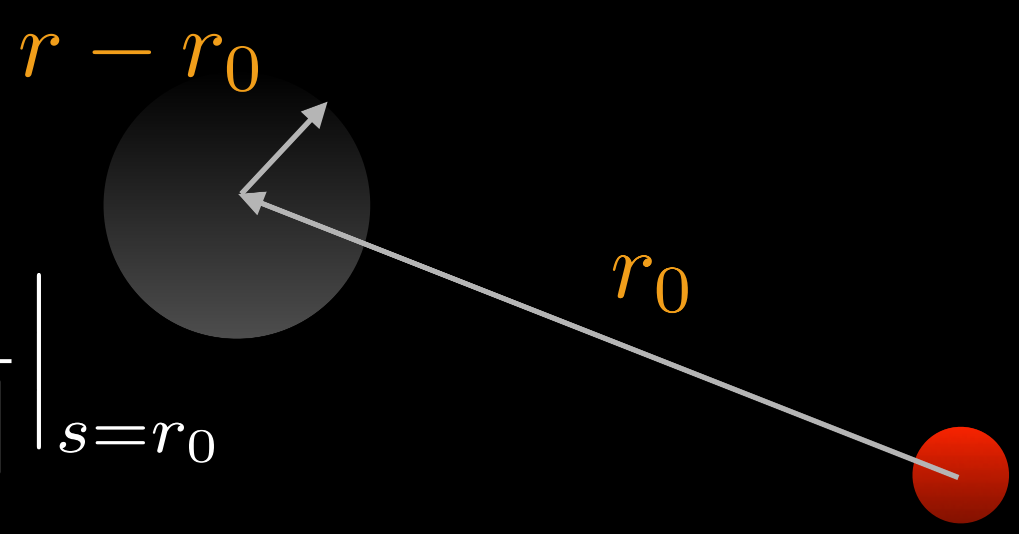
MULTIPOLES FROM REAL SPACE QUADRATURE

(SERM)ACS
Nashville, 2014

$$f(x) = f(0) + xf'(0) + \frac{x^2}{2}f''(0) + \ldots$$



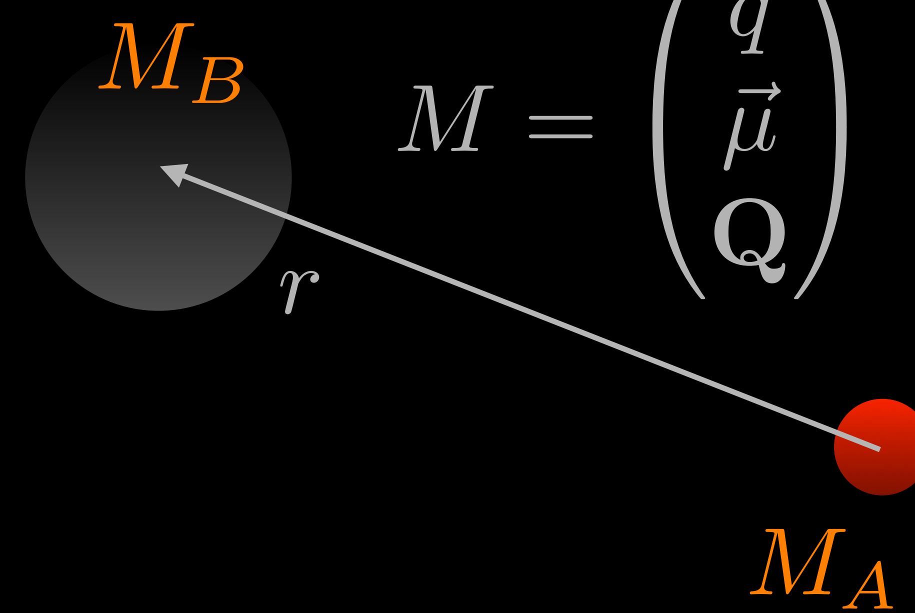
$$\Phi(r) = \sum_{n=0} \frac{((r - r_0)\cdot\partial_s)^n}{n!}\frac{1}{|s|}\Big|_{s=r_0}$$



WHAT IS A MULTIPOLE EXPANSION?

A coefficient.

$$V_{AB}^{\text{es}} = M_A \cdot T_{AB} \cdot \tilde{M}_B$$



$$M = \begin{pmatrix} q \\ \vec{\mu} \\ \mathbf{Q} \end{pmatrix}$$

FAR-FIELD INTERACTION E

- Potential function expansion
  - Transferable, Polarizable FFs
  - Fast multipole method, O(N)

$$T = \begin{bmatrix} r^{-1} & \partial r^{-1} & \partial^{(2)} r^{-1} \\ \partial r^{-1} & \partial^{(2)} r^{-1} & \partial^{(3)} r^{-1} \\ \partial^{(2)} r^{-1} & \partial^{(3)} r^{-1} & \partial^{(4)} r^{-1} \end{bmatrix}$$

Jacobson, Williams, Herbert, JCP 130, 2009.

$\partial^{(4)}_{\alpha\beta\gamma\delta}$ Cartesian: $3^4 = 81$ component tensor!

$$M_{lm} = \sum_i q_i |r_p|^l C_{lm}(\hat{r}_p)$$

$$V_{l,k} = \binom{2l+2k}{2l}^{1/2} R^{-l-k-1} \sum_{m=-l-k}^{l+k} (-1)^m C_{l+k,-m}(\hat{R}) [M_A^{(l)} \otimes \tilde{M}_B^{(k)}]_{l+k,m}$$

$$[M_A^{(l)} \otimes \tilde{M}_B^{(k)}]_{l+k,m} = \sum_{n=-l}^{l} \sum_{j=-k}^{k} M_{A,n}^{(l)} \tilde{M}_{B,j}^{(k)} \langle l, n; k, j | l+k, m \rangle$$

Jeziorski, Moszynski, Szalewicz, Chem. Rev. 94, 1994.

BUT IT'S NOT SO SIMPLE?

Spherical multipoles are efficient, yet unintelligible.

THE REAL PROBLEM

$$\frac{1}{|x-y|} = e^{-y\cdot\partial}\frac{1}{|x|}$$

$$= \sum_{l=0} \frac{|y|^l}{|x|^{l+1}} P_n(\hat{x}\cdot\hat{y})$$

$$= \sum_{l=0} \sum_{m=-l}^{l} O_{l,m}(x) M_{l,m}(y)$$

One step too far!

$$O_{lm}(x) = |x|^l (l+|m|)! P_{lm}(\cos\theta_x) e^{-im\phi_x}$$

$$M_{lm}(x) = |x|^{-l-1} (l-|m|)!^{-1} P_{lm}(\cos\theta_x) e^{im\phi_x}$$

White and Head-Gordon, JCP 101, 1994.

THE REAL PROBLEM

$$\frac{1}{|x-y|} = e^{-y\cdot\partial}\frac{1}{|x|}$$

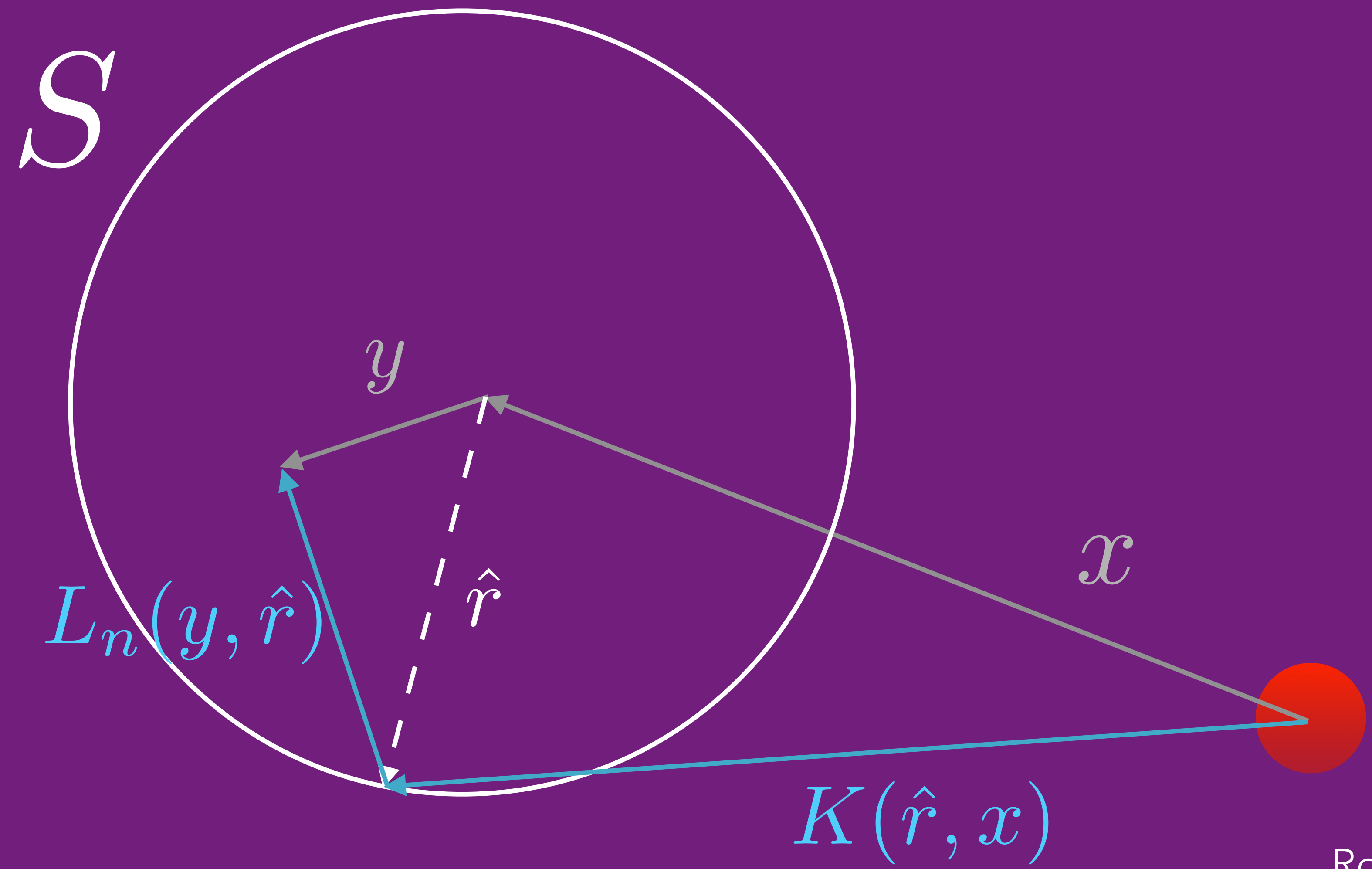
$$= \sum_{l=0} \frac{|y|^l}{|x|^{l+1}} P_n(\hat{x}\cdot\hat{y})$$

$$= \sum_{l=0} \frac{|y|^l}{|x|^{l+1} n!} \hat{x}^{(n)} \; {}_{(n)} \; \mathcal{T}_n \hat{y}^{(n)}$$

One step too far!

$$\partial^{(n)}|r|^{-1} = (-1)^n |r|^{-2n-1} \mathcal{T}_n r^{(n)}$$

Applequist, J. Phys. A, Math Gen, 22, 1989.



Rogers (submitted), 2014.

$$(-y \cdot \partial)^n |x|^{-1}/n! = L_n(y, x)$$ **directional derivative**

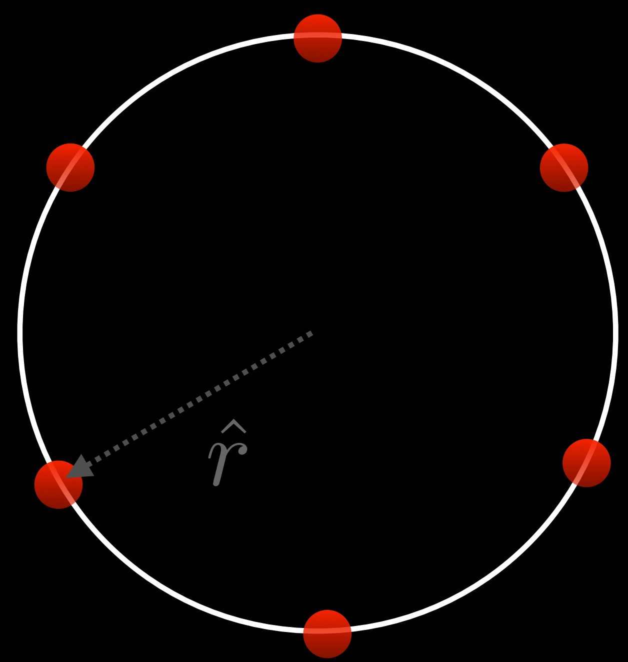
$$= \int_S L_n(y, \hat{r}) K(\hat{r}, x) \, d^2\hat{r}$$ **spherical projection**

BACK TO THE DRAWING BOARD.

Ahrens and Beylkin, Proc. Royal Soc. A, 465, 2009.

QUADRATURE

- Optimal number of points (p^2)
- Physical interpretation = surface charge distribution

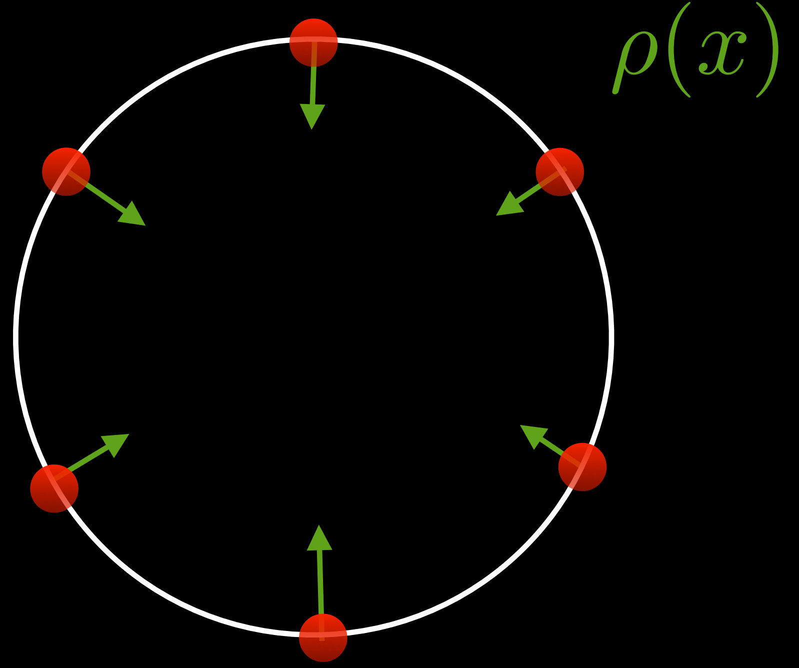


$$\int_S f(y,\hat{r})\sigma(\hat{r})\ d^2\hat{r}$$

$$= \sum_i \underbrace{(w_i \sigma(\hat{r}_i))}_{q_i} f(y,\hat{r}_i)$$

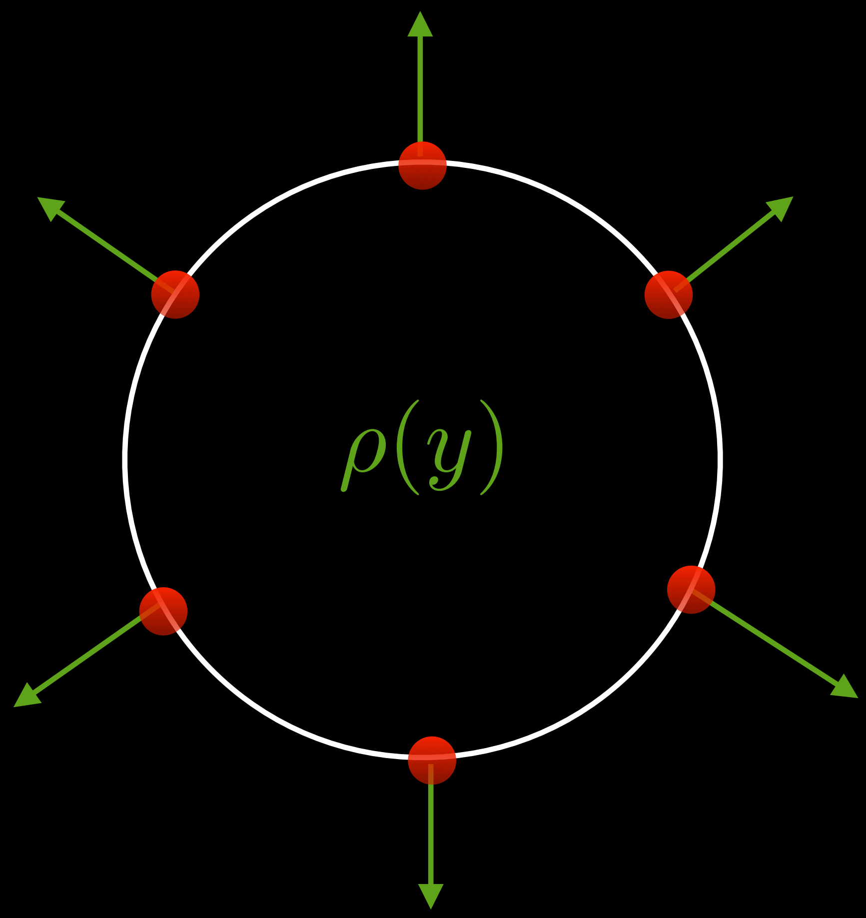
INNER EXPANSION

$$\sigma_i(\hat{r}) = \int K(\hat{r}, x)\rho(x)\; d^3x$$



OUTER EXPANSION

$$\sigma_o(\hat{r}) = \int \rho(y)K(y, \hat{r})\; d^3y$$



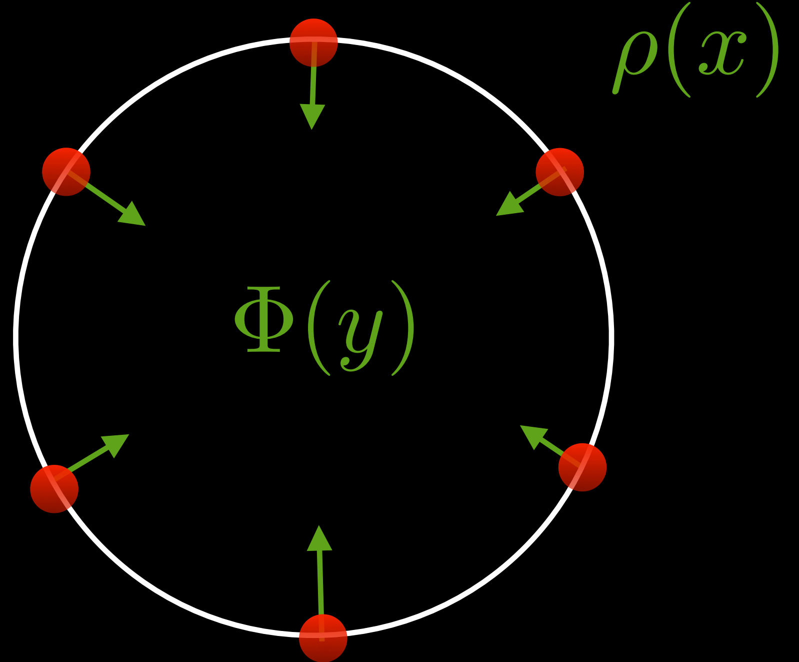
- Getting in is easy

INNER EXPANSION

$$\Phi(y) = \int_S \sum_n L_n(y, \hat{r})\sigma_i(\hat{r})\ d^2\hat{r}$$

$$\simeq \frac{q_i}{|y - \hat{r}_i|}$$

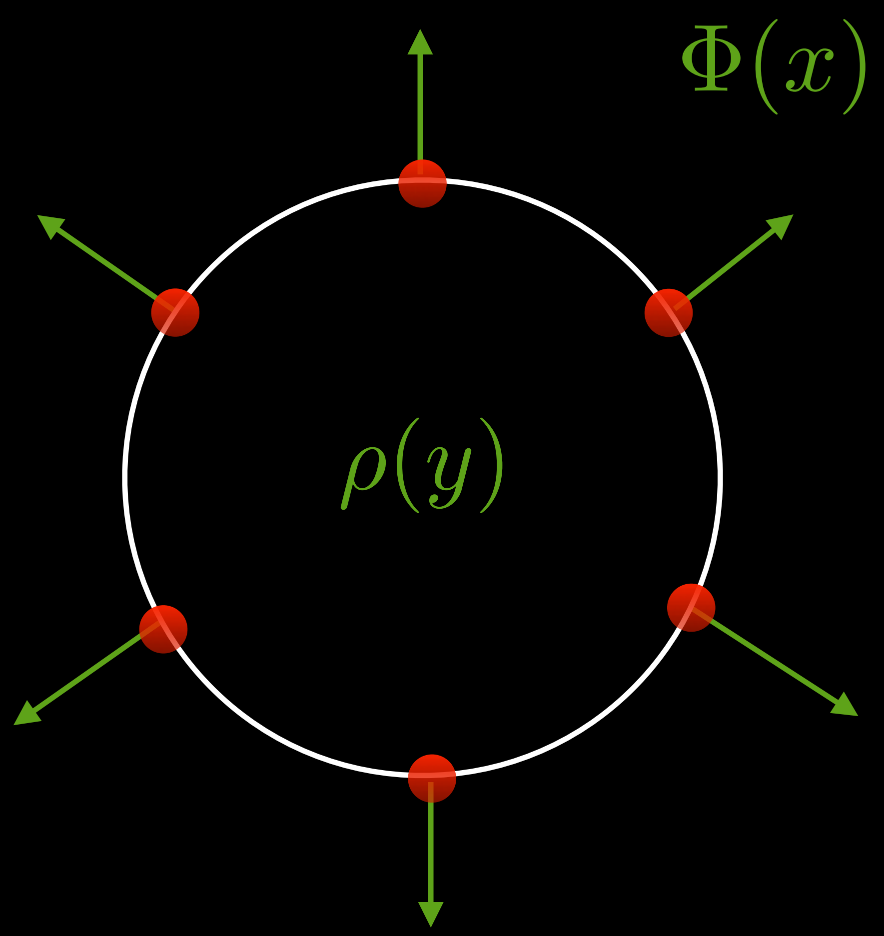
(may require scaling *S*)



OUTER EXPANSION

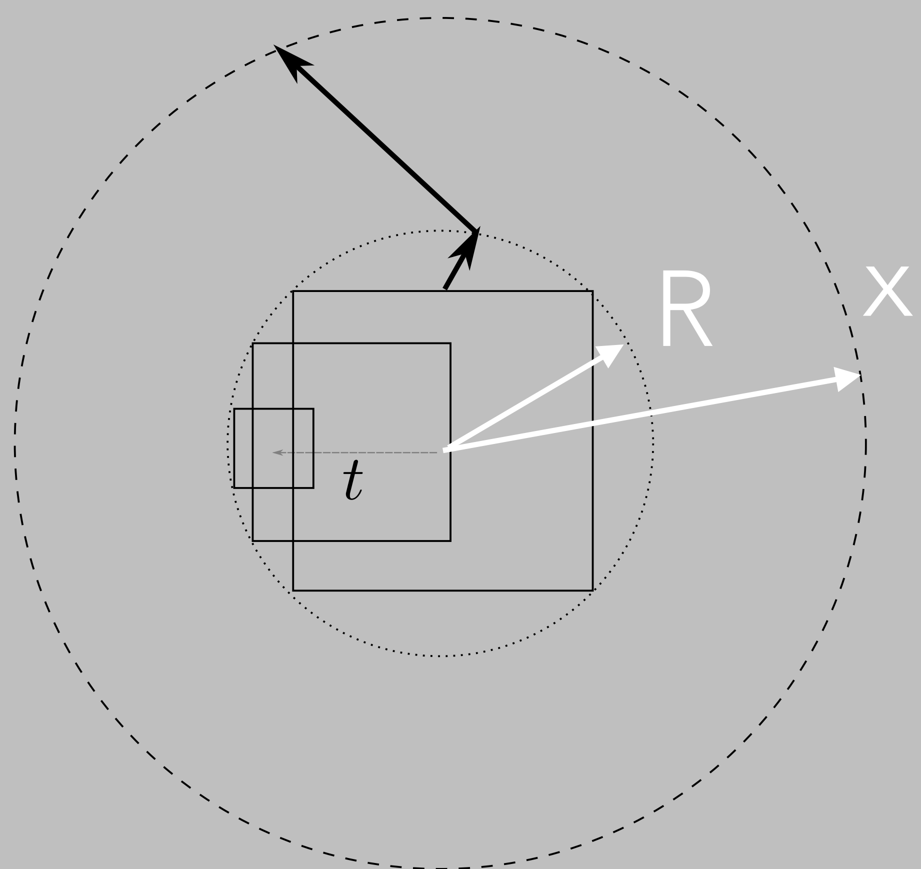
$$\Phi(x) = \int_S \sigma_o(\hat{r}) \sum_n L_n(\hat{r}, x)\ d^2\hat{r}$$

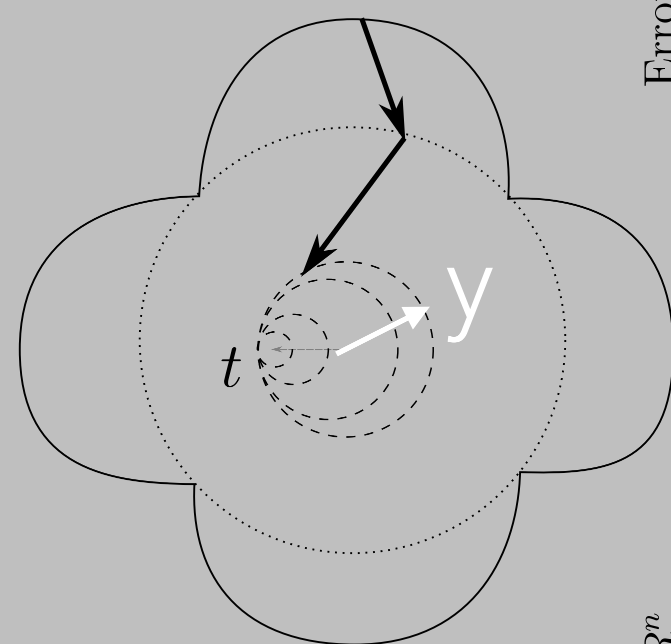
$$\simeq \frac{q_i}{|x - \hat{r}_i|}$$

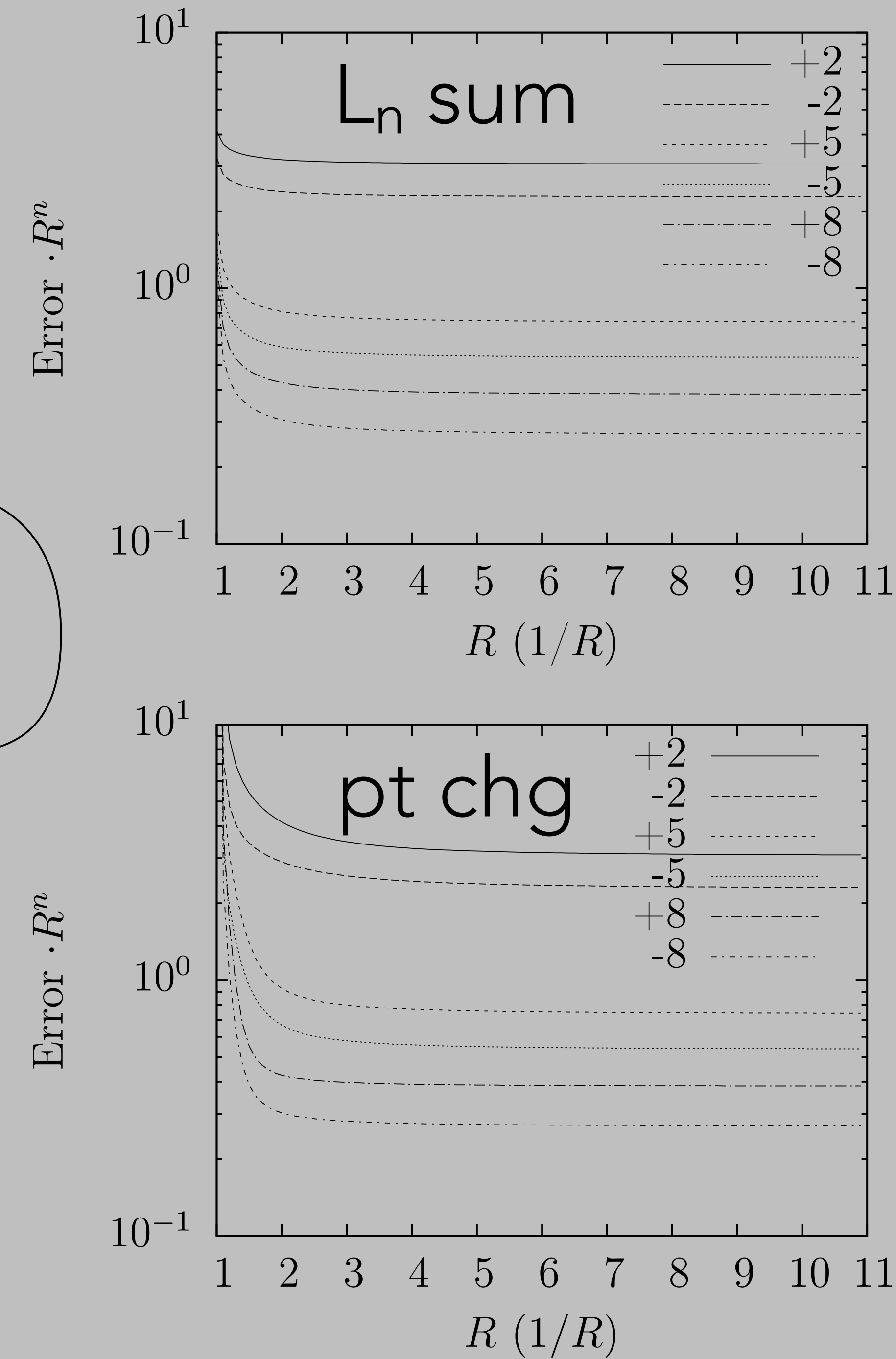


- Getting out is **even easier**!

ERROR?







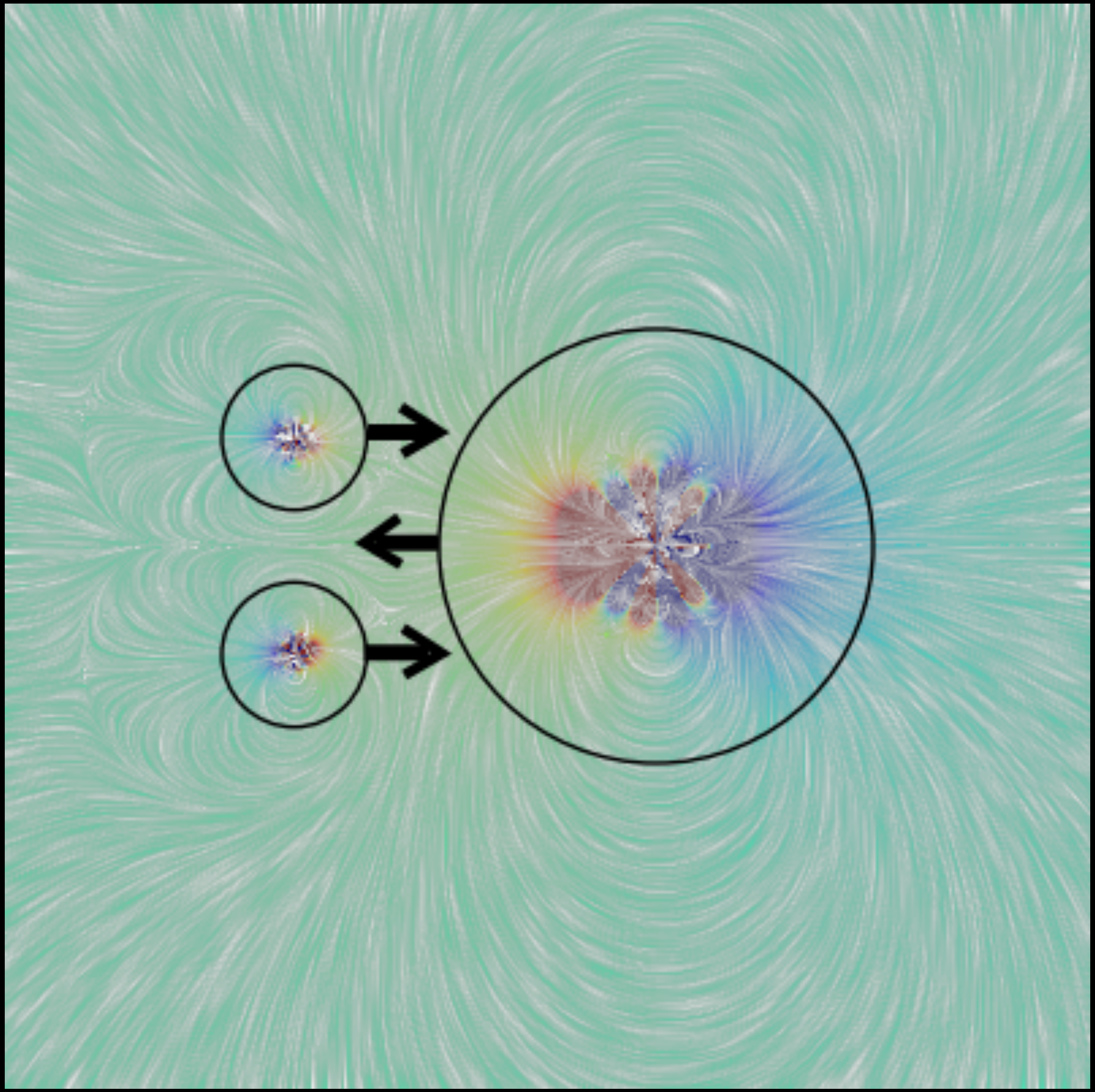
$$O\left(\frac{R}{x}\right)^{p+1}$$

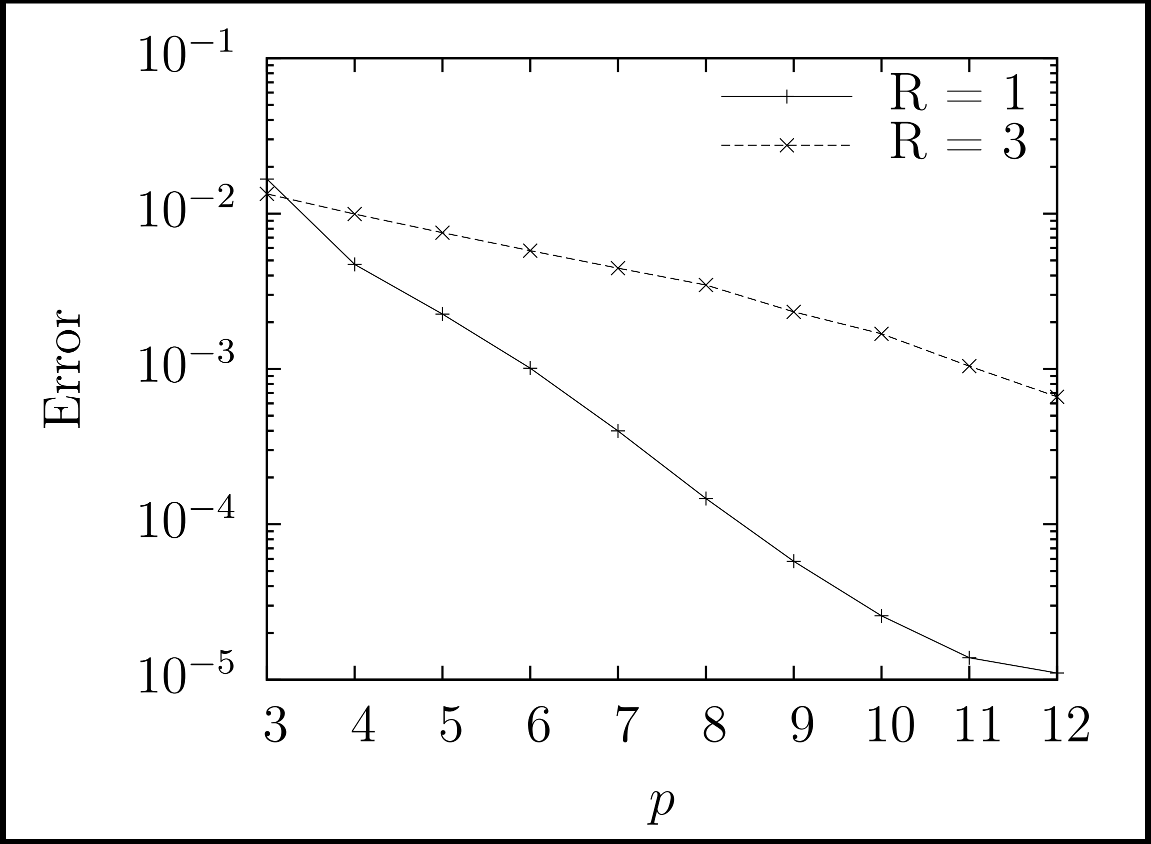
$$O\left(\frac{y}{R}\right)^{p}$$

Prefactor (au)

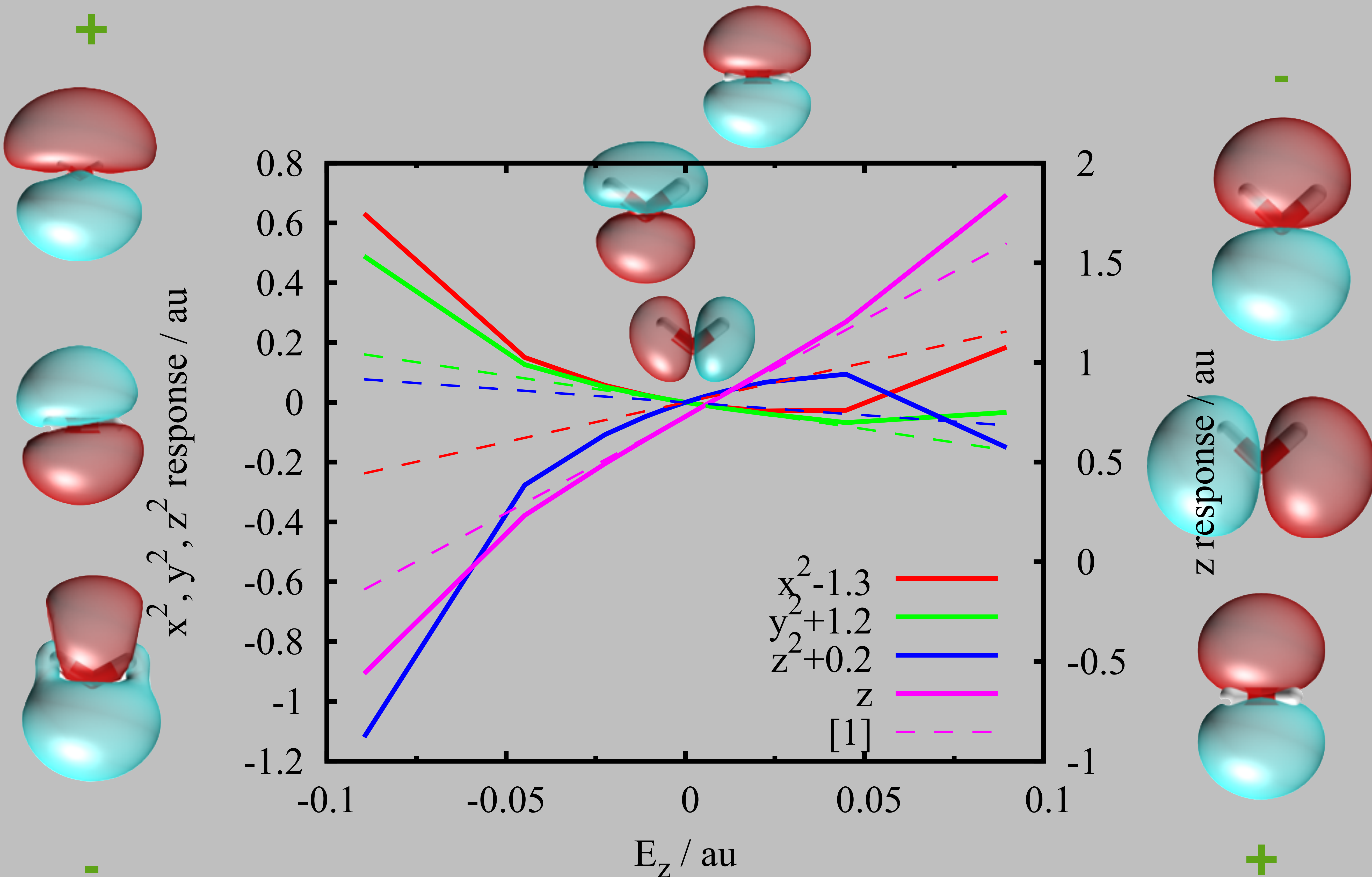
Rogers (submitted), 2014.

$$v(x) \equiv -\partial\Phi(x)$$
$$0 = \partial^2\Phi(x)$$
$$n \cdot v(x) = v_0(x), x \in \partial\Omega$$





FUN WITH MULTIPOLES



WORK WITH MULTIPOLES

[1] Elking et. al., J. Comput. Chem. 32, 2011.

CONCLUSIONS

- Spherical harmonics considered harmful
  - May have convergence issues!

    Makino, J. Comp. Phys. 151, 2009.
- Real-space Quadrature
  - Basis vectors are real
  - Weights are charges
  - Approx. power and dimension identical
  - Symmetry is apparent
  - Shifting functions are identical to initial fitting!

    Rogers (submitted), 2014.

ACKNOWLEDGMENTS

- University of South Florida Research Foundation
- Jaydeep Bardhan, Northeastern Univ.

USF UNIVERSITY OF SOUTH FLORIDA